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**CERAMIC-METAL BORE  
SEAL DEVELOPMENT**

*by P. E. Kueser, M. F. Parkman, and J. W. Toth*

*Prepared by*  
**WESTINGHOUSE ELECTRIC CORPORATION**  
Lima, Ohio  
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16. Abstract <p>A potassium-resistant bore seal capsule (4-in. O.D. by 4-in. high) was fabricated. The ceramic used was low-silica 99.8 percent beryllia, and the metal end bells were made from columbium-1 percent zirconium sheet. Joining was accomplished with an active-metal brazing alloy having a composition in weight percent of 60Zr-25V-15Cb. After fabrication the capsule was loaded with 4 grams of high purity potassium and sealed while in a vacuum chamber. The bore seal capsule was exposed for 5000 hours at 1300° F in an ion-pumped thermal vacuum chamber with pressures in the 10<sup>-9</sup> torr range. During this test exposure, the capsule remained potassium leak-tight. A variety of materials were tested during the program. Equipment and processes were developed for ceramic to metal brazing, brazement testing, and for alkali metal loading. A study was conducted on the outgassing characteristics of ceramics that had been fabricated by different methods. High purity alumina and beryllia ceramics (99.8% pure) and a series of brazing alloys were used in fabricating brazements. Selected brazements were evaluated for strength, leak tightness, and compatibility with potassium or lithium exposure at temperatures through 1600° F.</p> <p><i>170 p. Refs p. 170</i> <i>1. Salts (stoppers)</i></p>			
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## PREFACE

The work described herein was done under NASA Contract 3-6465. Mr. R. A. Lindberg, Space Power Systems Division, NASA Lewis Research Center, was the Project Manager for this program.

The Westinghouse Electric Corporation Aerospace Electrical Division (WAED) performed the work reported herein, with contributions from the EIMAC Division of Varian Associates in the preparation and test of bore seal materials. P. E. Kueser, Manager, Materials Development, WAED, was the Program Manager. J. W. Toth (WAED) and M. F. Parkman and R. C. McRae (EIMAC) were the principal investigators.

Contributors and consultants who actively participated on this project were R. P. Shumate, W. L. Grant, and H. J. Krause of WAED and L. Reed and R. Hofheins of EIMAC.



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## SECTION I

### INTRODUCTION AND SUMMARY

This report presents the results of a potassium-resistant bore seal development program. The bore seal development program culminated in the fabrication of a 4-inch outside diameter by 4-inch high bore seal capsule. The ceramic used was low-silica 99.8 percent beryllia and the metal end bells were made from columbium-one percent zirconium sheet. Joining was accomplished with an active-metal brazing alloy having a composition in weight percent of 60Zr-25V-15Cb. After fabrication the capsule was loaded with four grams of high purity potassium and sealed while in a vacuum chamber. The bore seal capsule was exposed for 5000 hours at 1300° F in an ion-pumped thermal vacuum chamber with pressures in the  $10^{-9}$  torr range. During this test exposure, the capsule remained potassium leak-tight.

The program leading to the development of the bore seal capsule included testing of a variety of materials. Equipment and processes were developed for ceramic to metal brazing, brazement testing, and for alkali metal loading. A study was conducted on the outgassing characteristics of ceramics that had been fabricated by different methods. High purity alumina and beryllia ceramics (99.8% pure) and a series of brazing alloys were used in fabricating brazements. Selected brazements were evaluated for strength, leak tightness, and compatibility with potassium or lithium exposure at temperatures through 1600° F.

## SECTION II

### BORE SEAL DEVELOPMENT

#### A. INTRODUCTION

This bore seal development program continued the work initiated and reported under NAS3-4162 (Ref. II-1)<sup>1</sup>. Ceramic-to-metal seal systems that were previously found promising after exposure to potassium or lithium were subjected to longer duration tests. Alkali metals were loaded into specimen test capsules in a vacuum environment on this program, where as previously, they were loaded under a high-purity argon cover gas. Active metal brazing of ceramics to columbium-1% zirconium (Cb-1Zr) was investigated. The resulting brazements had less-brittle metallurgical structures than previously used brazes that had refractory-metal metallizing containing a thermodynamically stable second phase (ref. II-1). More ductile ceramic-to-metal joints are necessary to accomodate increased stresses and thermal mismatch to be encountered in larger size bore seals for future requirements( 4- to 28-inch diameter).

An evaluation of the metallurgical structure of several brazed seal systems was made. The best active-metal braze alloys found on the previous program and new active-metal braze alloys were evaluated using modulus-of-rupture specimens for flexural strength determination on this program. Tab peel specimens were evaluated for brittleness and notch sensitivity. One-half-inch diameter ceramic tubes were joined to a Cb-1Zr metal member to determine vacuum leak-tightness. Tests and evaluations of these configurations were made before and after exposure to alkali-metal vapor and liquid at 1600° F for time periods to 2000 hours. The ceramic bodies under investigation included those which previously survived 500-hour exposure to alkali metals at 1600° F and several new candidate compositions containing beryllia or yttria. An outgassing study was conducted on several ceramic bodies to determine whether special conditioning would be required to prevent contamination of potassium by deleterious outgassed products. Two-inch diameter ceramic-to-metal seals were fabricated and subjected to thermal cycling and vibration tests. Elevated temperature flexural strength and vacuum integrity were determined on an active-metal brazed seal system which was found to be suitable for 1600° F potassium exposure.

A four-inch diameter ceramic to columbium-1% zirconium bore seal capsule was designed and fabricated utilizing a braze alloy selected from those developed on the previous program. This bore seal capsule was both loaded with four grams of high-purity potassium and sealed in a vacuum and was endurance tested in a stator

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<sup>1</sup>References are listed at the end of this report.

cavity for 5000 hours at 1300° F. No evidence of any degradation was found in this test (ref. II-2).

## B. EQUIPMENT AND EXPERIMENTAL PROCEDURES

Uncombined oxygen available to potassium will combine with the potassium and thereby greatly increase the potassium's corrosive effects (refs. II-3 and II-4). Care must therefore be taken to minimize oxygen contamination: (1) during test assembly fabrication, (2) during alkali metal handling, and (3) during elevated temperature testing. One approach to minimizing oxygen contamination was described previously (ref. II-1). Modifications in this equipment, new equipment, and new or changed procedures are described in this section. General cleaning and brazing procedures are detailed in Section II of Appendix A of this report. Also described in this section are the equipment and procedures used in performing a variety of physical and thermal tests on ceramic-to-metal brazed joint assemblies.

### 1. Modification of the Test Capsule Loading and Welding Facility

A 25-cubic-foot glove box utilized previously (ref. II-1) for loading high-purity potassium into test capsules under inert gas was modified to permit loading under vacuum with subsequent capsule closure by electron-beam welding. The major modifications of the capsule welding and loading system included installation of a six-inch NCR 1500-liter per second oil diffusion pump and a Freon-cooled CVC trap (see figure II-1). A Brad-Thompson Industries Model 785 electron-beam welder (see figure II-2) was installed in the chamber with accessories required for part movement. The welder was powered by a Brad-Thompson Industries Model 1615.0 6-kW power supply. Glove ports were sealed and Materials Research Corporation Model V4-120 manipulators were installed so that all potassium loading, assembling and electron-beam welding operations could be conducted in vacuum. Polyethylene sleeves were placed over the manipulator fittings and control arm (figure II-3). By maintaining high-purity argon in these sleeves, the possible leakage of oxygen through the manipulator seals when they are subjected to a heavy load is reduced.

#### a. ELECTRON-BEAM WELDER

The electron-beam welder, described above, performed adequately in sealing Cb-Izr test capsules and no weld failures occurred during the course of this program. However, some problems were encountered thereby requiring refilling of test capsules and thus causing a delay in the program. Arc-over in the gun assembly, caused by excessive potassium vaporization, twice resulted in



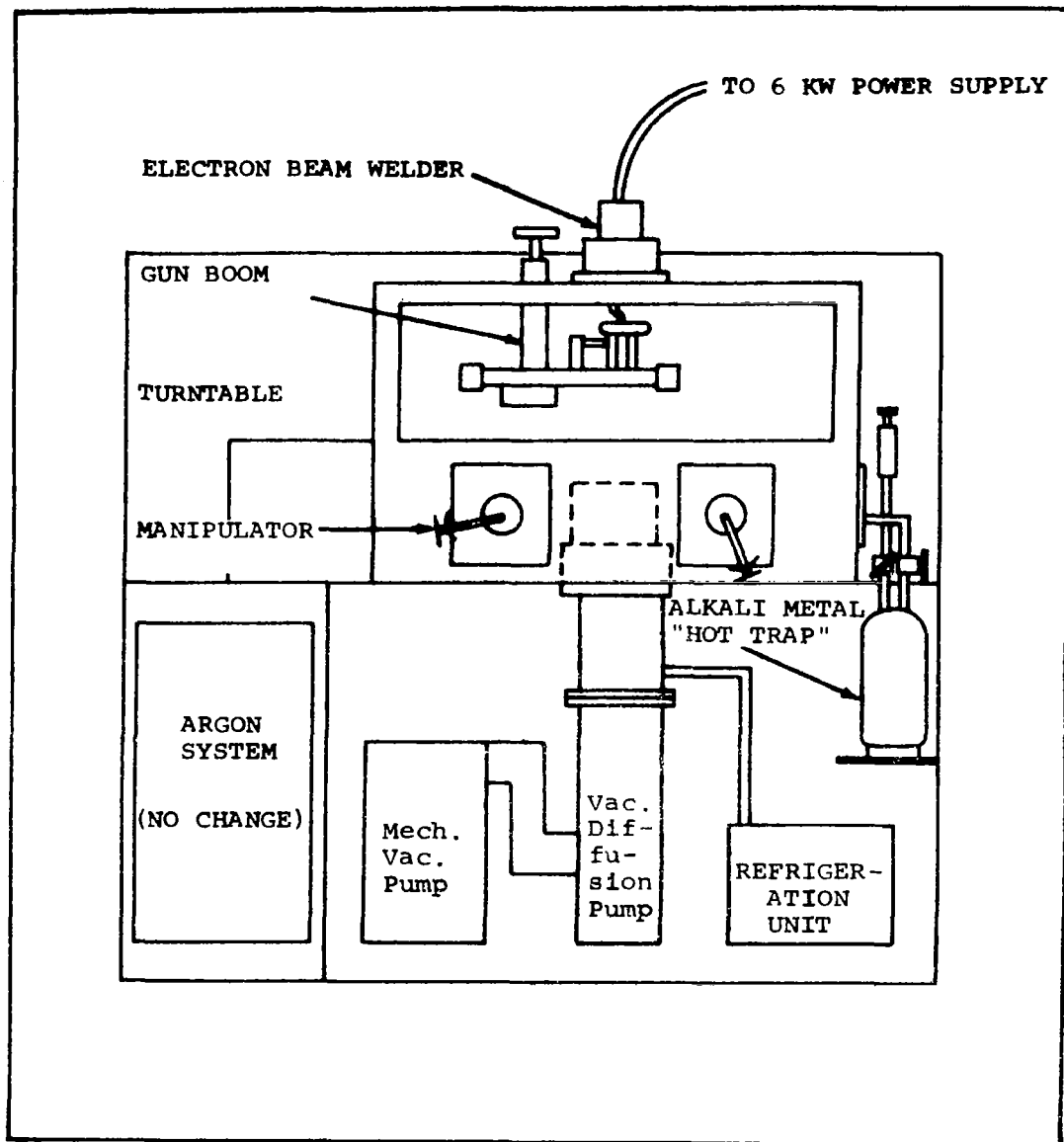


FIGURE II-1. Schematic of the Capsule Fabrication and Loading Equipment

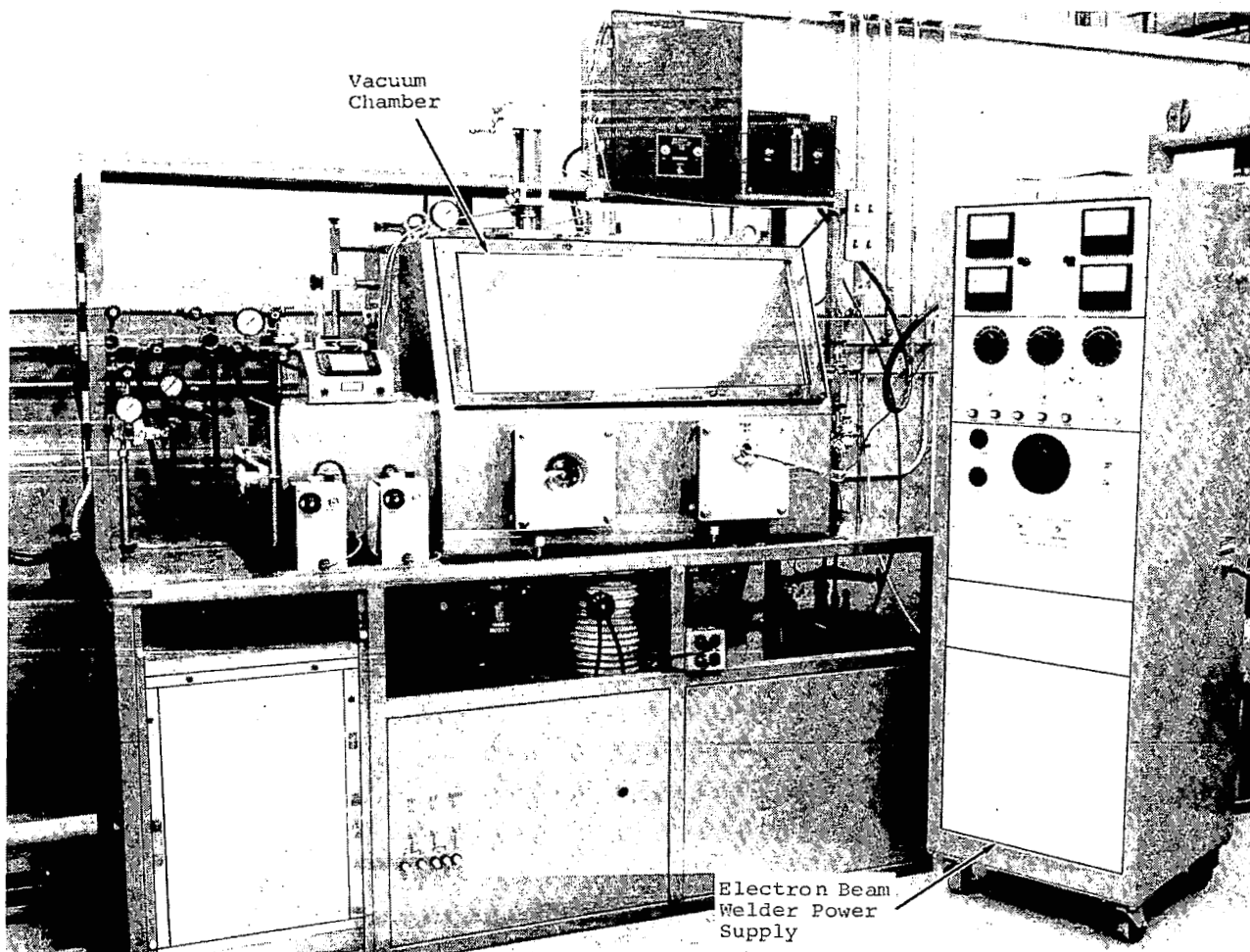


FIGURE II-2. Vacuum Chamber and Power Supply for Capsule Loading and Welding

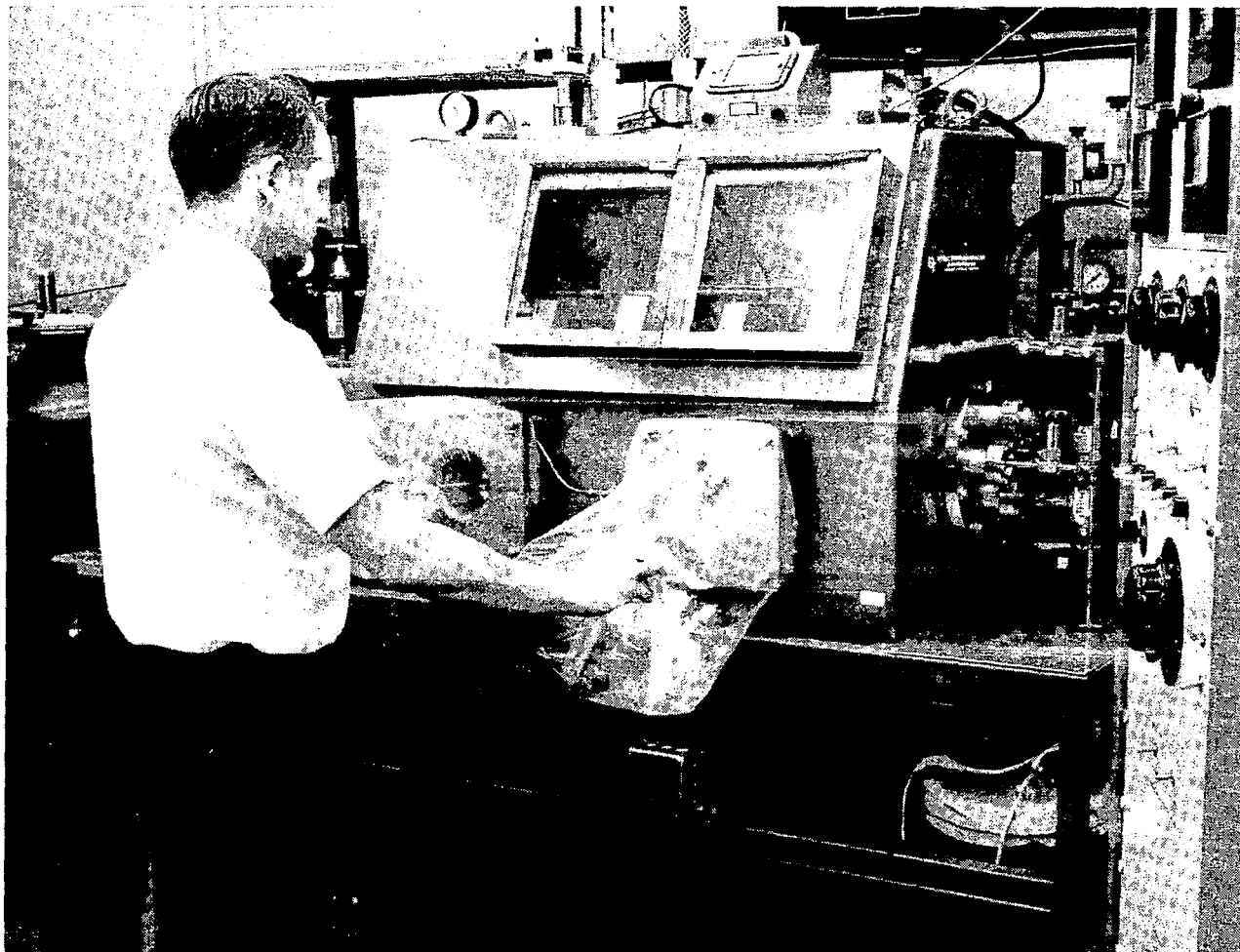


FIGURE II-3. Photograph Showing Arrangement of Argon Pressurized Polyethylene Sleeves Over Loading Chamber Manipulator Fittings and Handles

burned-out focus coils. Occasional gas bursts during welding caused a current surge thereby shutting off the welder. When this was caused by vaporized potassium, the weld closure generally could not be completed. Automatic current control would have alleviated this problem.

b. TEST CAPSULE DESIGN AND ALKALI-METAL LOADING PROCEDURE

Columbium-1% zirconium test capsules were modified from those used previously (ref. II-1), (figures II-4 and II-5) to aid in handling by manipulators and for easier closure by electron-beam welding. Chill blocks (figure II-6) were designed to keep the potassium cool during welding as well as to facilitate the transfer of capsules.

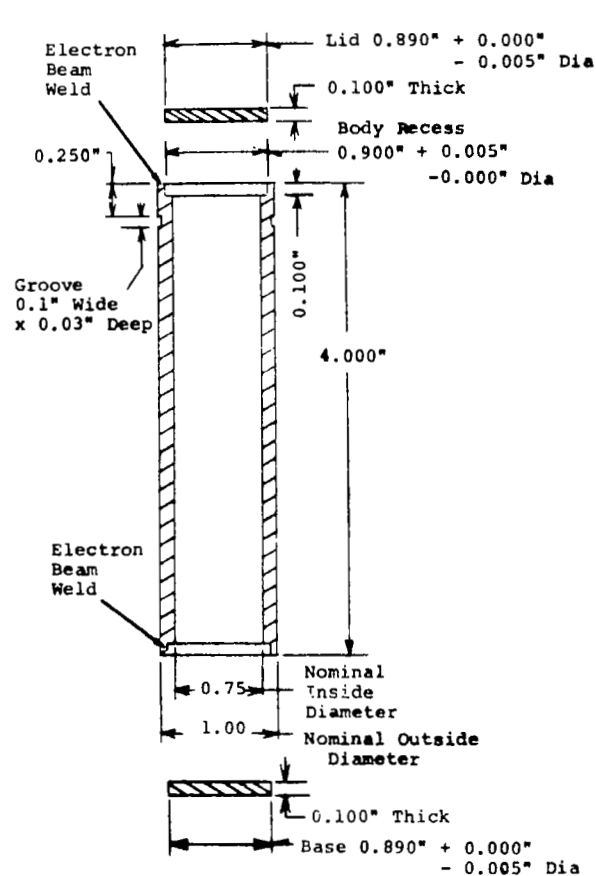
All heavy jigs or fixtures which were to be handled in the electron-beam welding chamber with the manipulators were reworked by adding pins which protruded horizontally from the top, 180 degrees apart (figure II-6). The manipulator jaws were fitted with vertical pins at the top of each jaw (figure II-6). These pins allowed the heavy items in the chamber to hang vertically during handling; thereby permitting better positioning into holes or on vertical pins, as required. The heavy (up to 2.5 pounds) chill block fixtures could thus be handled without putting excessive stress on the manipulator vacuum fittings. In practice, no pressure rise over  $9 \times 10^{-6}$  torr was attributable to the manipulators.

Three different test capsules were used on this program as shown below.

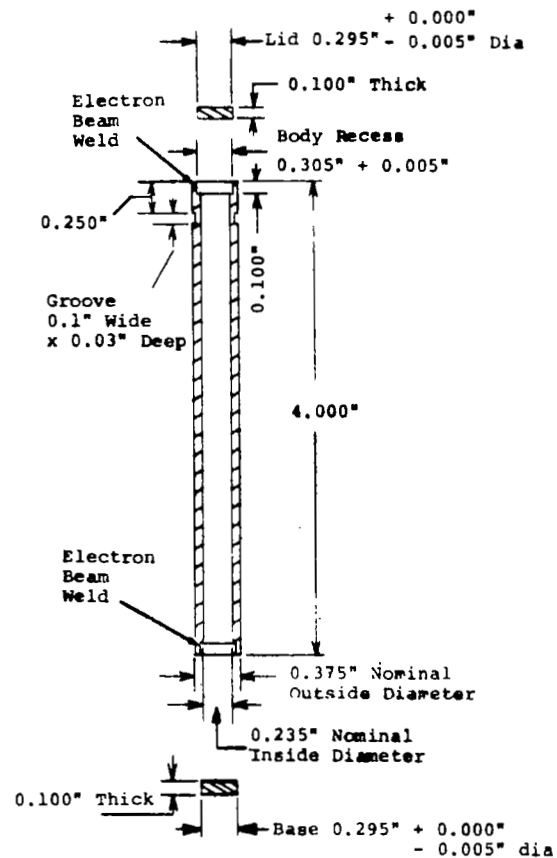
ITEM	MATERIAL	USE
MSAR <sup>2</sup> Purity Capsule, 0.375-inch O.D. by 4 inches long, with a 0.035-inch-thick wall.	Cb-1Zr	To transport alkali metal samples to MSAR; Potassium sample for O <sub>2</sub> analysis by Hg amalgamation; Li sample for N <sub>2</sub> analysis by the Kjeldahl method.
GA <sup>3</sup> Purity Capsule, 0.625-inch O.D. by 2 inches long, with a 0.020-inch-thick wall; supplied by GA.	Low oxygen type 304 stainless steel	To transport potassium sample to GA for O <sub>2</sub> analysis by neutron activation.

<sup>2</sup>Mine Safety Appliance Research, Callery, Pennsylvania

<sup>3</sup>General Atomics Division of General Dynamics, Inc., San Diego, Calif.



Exposure Type Capsule  
Material: Cb-18Zr



Purity Type Capsule  
Material: Cb-18Zr

FIGURE II-4. Test Capsule Design

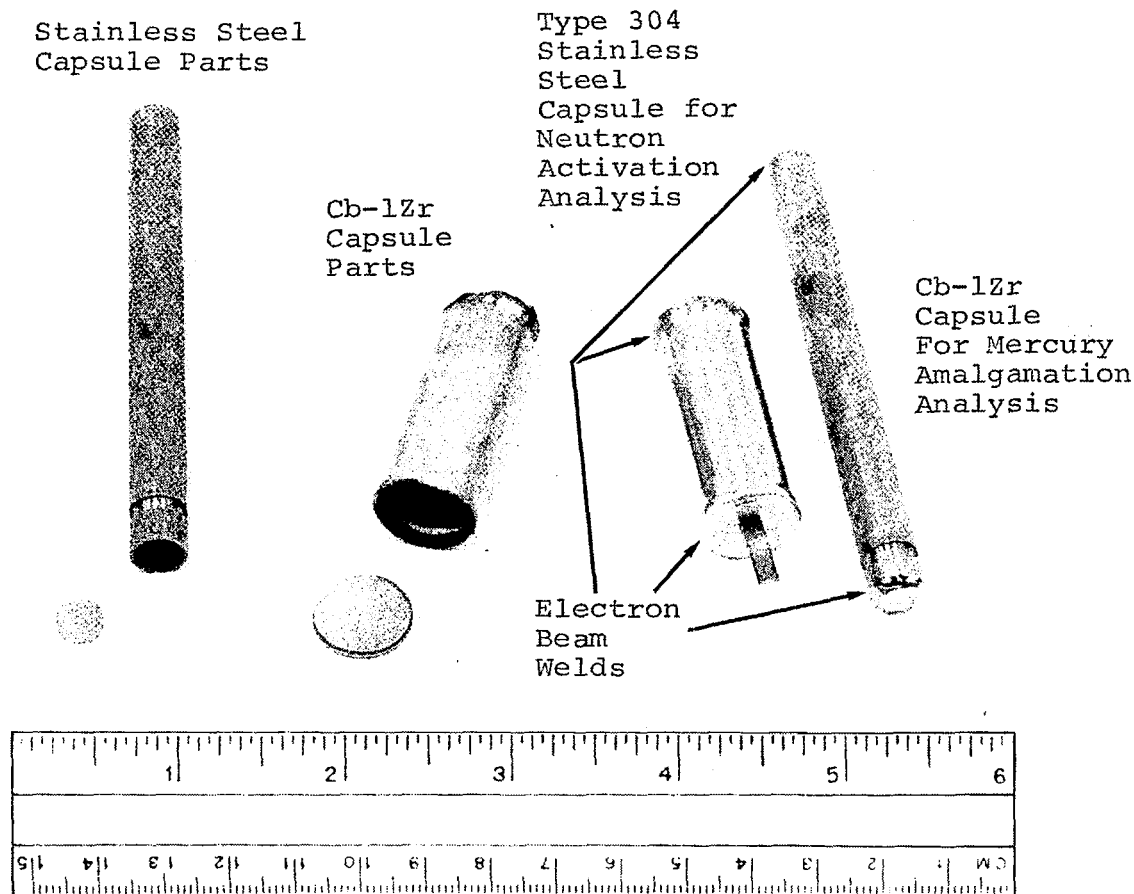


FIGURE II-5. Columbium-1% Zirconium and Stainless Steel Capsules for Mercury Amalgamation and Neutron Activation Analyses of Alkali Metals, Showing Electron Beam Weldments

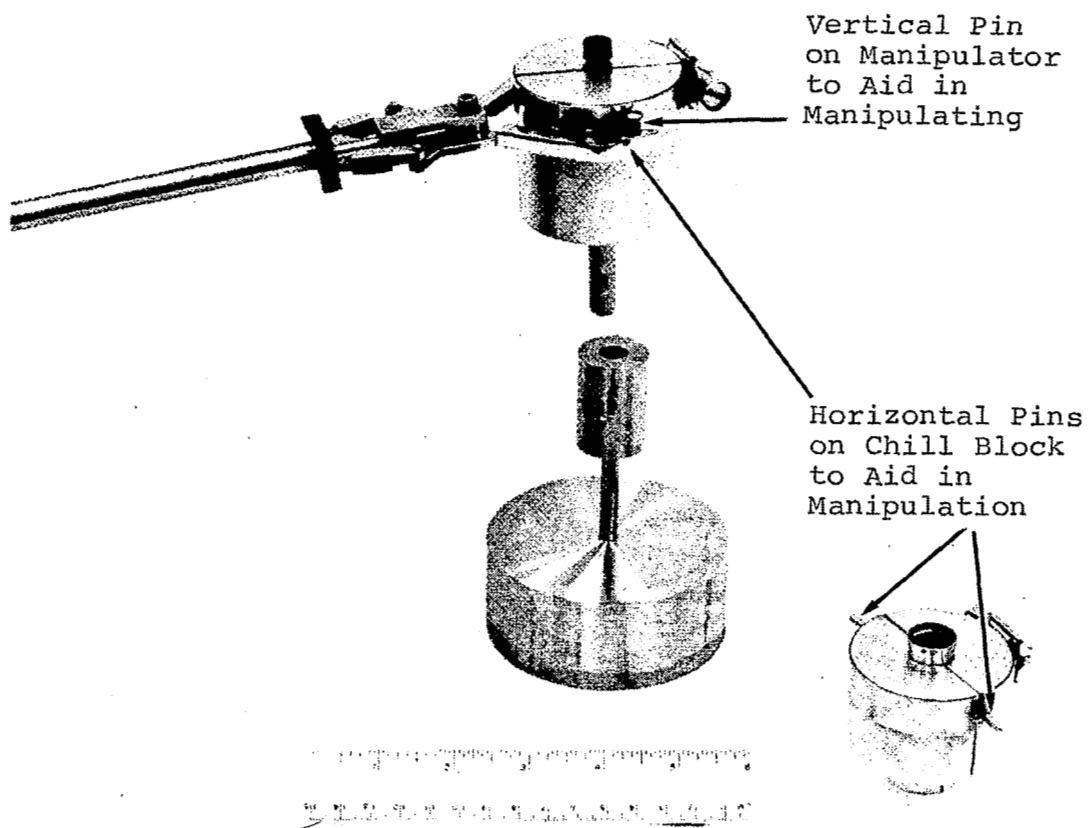


FIGURE II-6. Photograph of Manipulator Handling of Purity Test Capsule with Electron Beam Welder Chill Block Fixturing

ITEM	MATERIAL	USE
Exposure Test Capsule 1.00-inch O.D. by 4 inches long with a 0.125-inch-thick wall.	Cb-12r	To contain potassium or lithium and ceramic- to-metal brazements samples for compat- ibility tests.

Capsules were vacuum fired to 1100° F at  $<5 \times 10^{-6}$  torr to eliminate excessive outgassing during electron-beam welding and to remove uncombined oxygen. The detailed procedure adopted for filling capsules with alkali metal is given in Appendix B. Variations from this procedure were made and are outlined with the discussion of the pertinent tests.

A number of problems were encountered during loading in early loadings. A description of these follow:

- 1) Potassium solidified on the inside surface of the capsule during filling, thus bridging the tube opening. This resulted in an overflow before the desired amount of potassium had been loaded. The problem was resolved by preheating the capsule and chill block with a defocussed beam from the electron beam welder. About 180 watts of power applied for 7 minutes was found to be adequate.
- 2) Fit-up of the neutron activation purity test capsule parts was inadequate for reliable welding. Modification of the capsule to have its rim above the lid and use of a slightly defocussed beam resulted in successful closures.
- 3) Results from early neutron activation analyses disclosed that the oxygen content of the empty neutron activation test capsules was higher than desired.

#### c. CHECKOUT AND PROOF TESTING OF CAPSULE LOADING

A requirement to demonstrate that the alkali-metal handling and loading equipment and procedure were adequate was fulfilled by loading trial capsules and having the alkali-metal contents analyzed. Capsules loaded with potassium and lithium were found to contain less than 10 ppm oxygen and less than 40 ppm nitrogen respectively.

A series of capsule loadings were made. Potassium and lithium having specifications as listed in Appendix B were obtained from Mine Safety Appliance Research Corporation. The MSAR tanks contained zirconium getter material



and were attached directly to the electron-beam welding chamber to act as a combined hot trap and storage container.

Neutron activation analysis for oxygen in potassium was initially thought to be a method more satisfactory than the mercury amalgamation method. Early evaluation of trial loadings was based on neutron activation analyses only, although capsules for both types of analyses had been loaded. Later it was realized that the relatively high oxygen content of the neutron activation capsule's stainless steel was responsible for anomalous results. The final acceptance of a loading procedure was based on the mercury amalgamation method for oxygen determination.

After several trial loadings of gettered potassium into the test capsules, oxygen content of the potassium was analyzed and found to be less than 10 ppm by the mercury amalgamation method. The facility and procedures were then considered ready for specimen loading and testing. During the course of these trial loadings several significant observations were made.

- 1) Purging the potassium fill line, which extends from the hot-getter container to the interior of the vacuum chamber, reduced contamination. Flushing of the fill-line and tip with hot potassium just prior to loading aided even more significantly in the reduction of oxygen contamination.
- 2) The installation of polyethylene sleeves over the vacuum manipulator fittings and handles reduces the possibility of potassium contamination during loading. The sleeves were pressurized with high-purity argon during service. This modification is especially useful if heavy accessories in the vacuum chamber are lifted and moved with these manipulators.
- 3) The potassium hot-trap container is an effective method of storing and gettering potassium. After intermittent use over a period of 18 months and frequent hot-gettering cycles, the potassium remaining in the container was analyzed before refilling with a second lot (B) of potassium. The oxygen content of the remaining potassium was less than 10 ppm. Analysis was performed by the mercury amalgamation method by Mine Safety Appliance Research Corporation.

- 4) Loading capsules with lithium proved more difficult than with potassium. The purity of the best starting material from commercial sources and the analysis methods are not adequate for providing lithium suitable for long-term, high-temperature testing.

## 2. Vacuum Furnace for the High Temperature, Long-Term Exposure of Test Capsules

To assure pressure in the  $10^{-9}$  torr range during the 2000-hour,  $1600^{\circ}$  F exposure of Cb-1Zr test capsules containing test specimens and alkali metal, the dual vacuum furnace (ref. II-1) was modified (figure II-7) as follows: the diffusion pumping system was replaced with an Ultek No. 20-365, 400-liter-per-second ion pump and power supply. The bell jar O-ring flanges were replaced with ultra-high-vacuum gold seal flanges. The same manifold and furnace structure (figures II-8 and II-9) as previously described (ref. II-1) was used. The system is roughed with a portable Welch 1397B forepump through a 1/2-inch copper tubulation at the top center flange. The tubulation is nipped off after starting the sputter-ion pump. After a mild bakeout with heating tapes and lamps overnight, the cold, dry, and empty system reached a pressure of  $8 \times 10^{-10}$  torr.

## 3. Ceramic Outgassing Equipment and Procedure

The investigation of outgassing of bore seal ceramics was undertaken to learn whether an outgassing step was necessary to prevent contamination of potassium by the outgassed components.

Alumina and beryllia ceramics are usually fabricated by sintering the appropriate powders in compacted form, in an oxidizing atmosphere for 1/2 to 3 hours at temperatures in the  $2700^{\circ}$  to  $3100^{\circ}$  F range. Dissolved, chemisorbed, and occluded oxygen-containing gases ( $H_2O$ , CO,  $CO_2$ ) are, therefore, released by the ceramics during subsequent treatment or use at elevated temperatures. Previous work (ref. II-5) at EIMAC Division of Varian Associates on alumina and sapphire outgassing had shown that cleaning and heat treating procedures on as-received ceramics also markedly affect the outgassing rate and the composition of the gas volume evolved.

The outgassing studies cited consist of heating the samples from temperature  $T_1$  to temperature  $T_2$  in a vacuum furnace, collecting the evolved gases, and then analyzing them with a mass spectrometer. The method was useful in determining the total evolved gas content and composition for the  $T_1$  to  $T_2$  heat treatment. Subsequently, a technique and associated instrumentation was developed at EIMAC which offered the

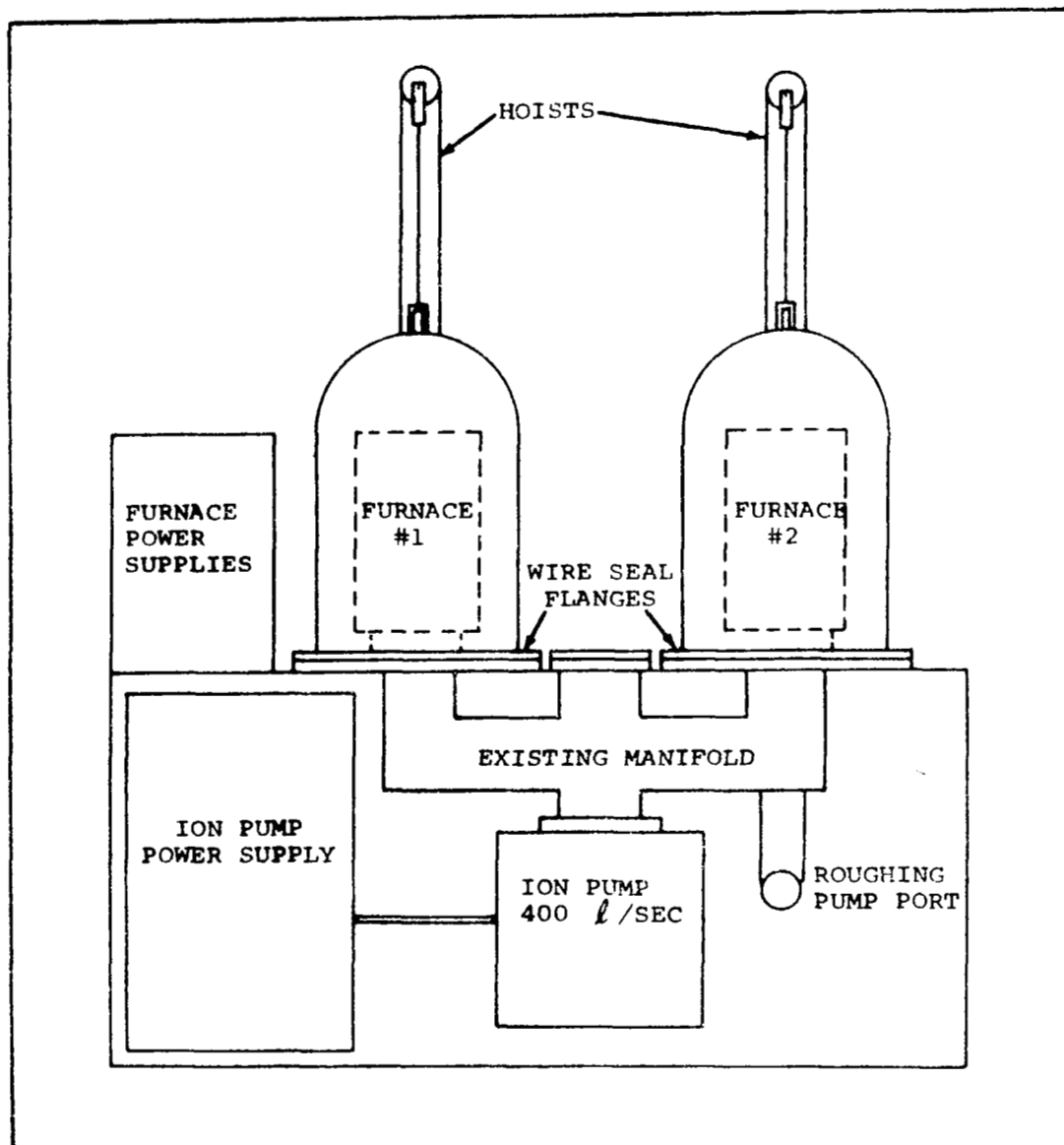


FIGURE II-7. Schematic of Dual Vacuum Furnace Modifications Using Ion Pumping

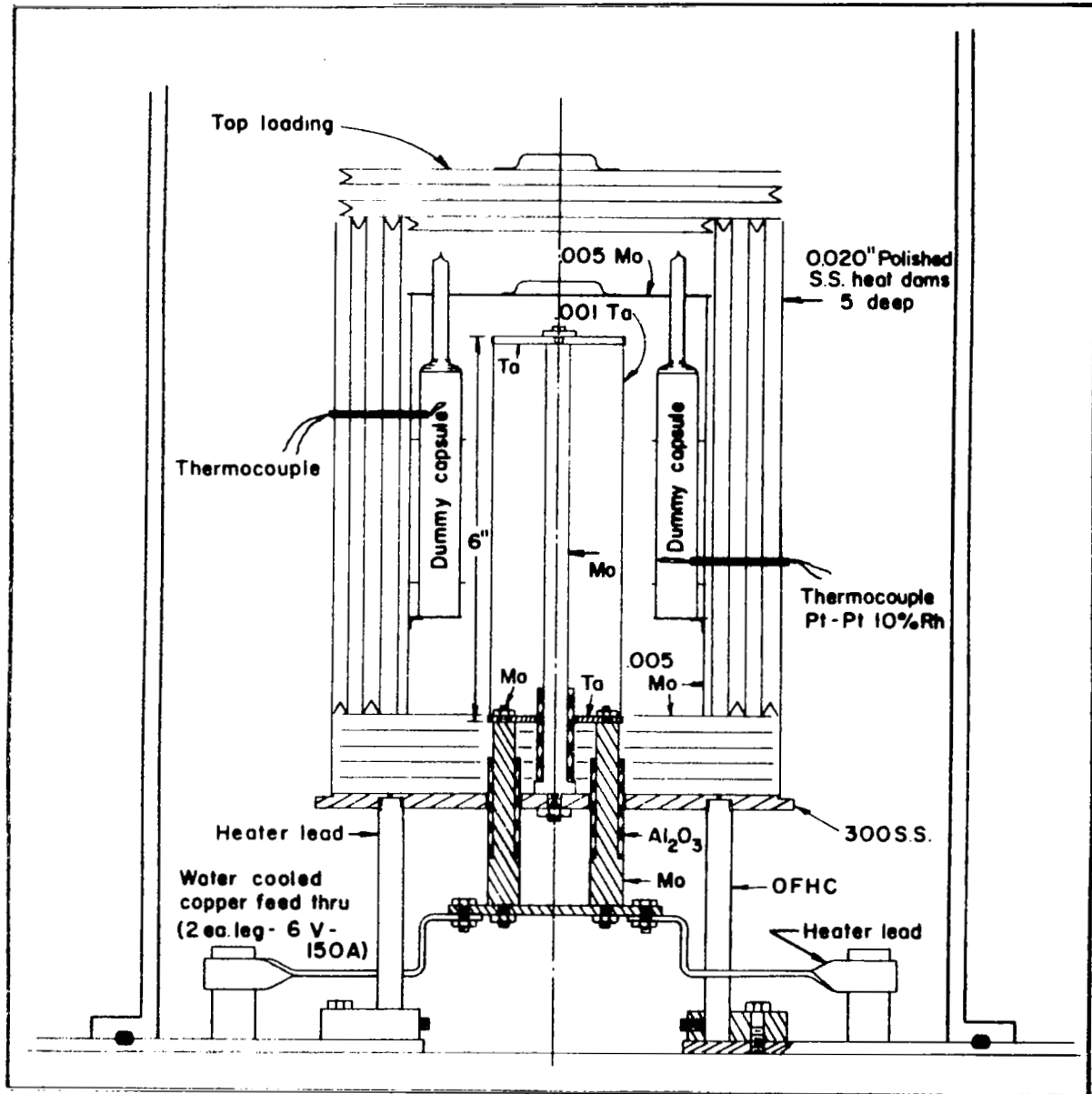


FIGURE II-8. Schematic of Tantalum Element Vacuum Furnace Used in 1000° and 1600°F Capsule Exposure Tests. Dummy Capsules Contain Thermocouples Used to Monitor Temperature

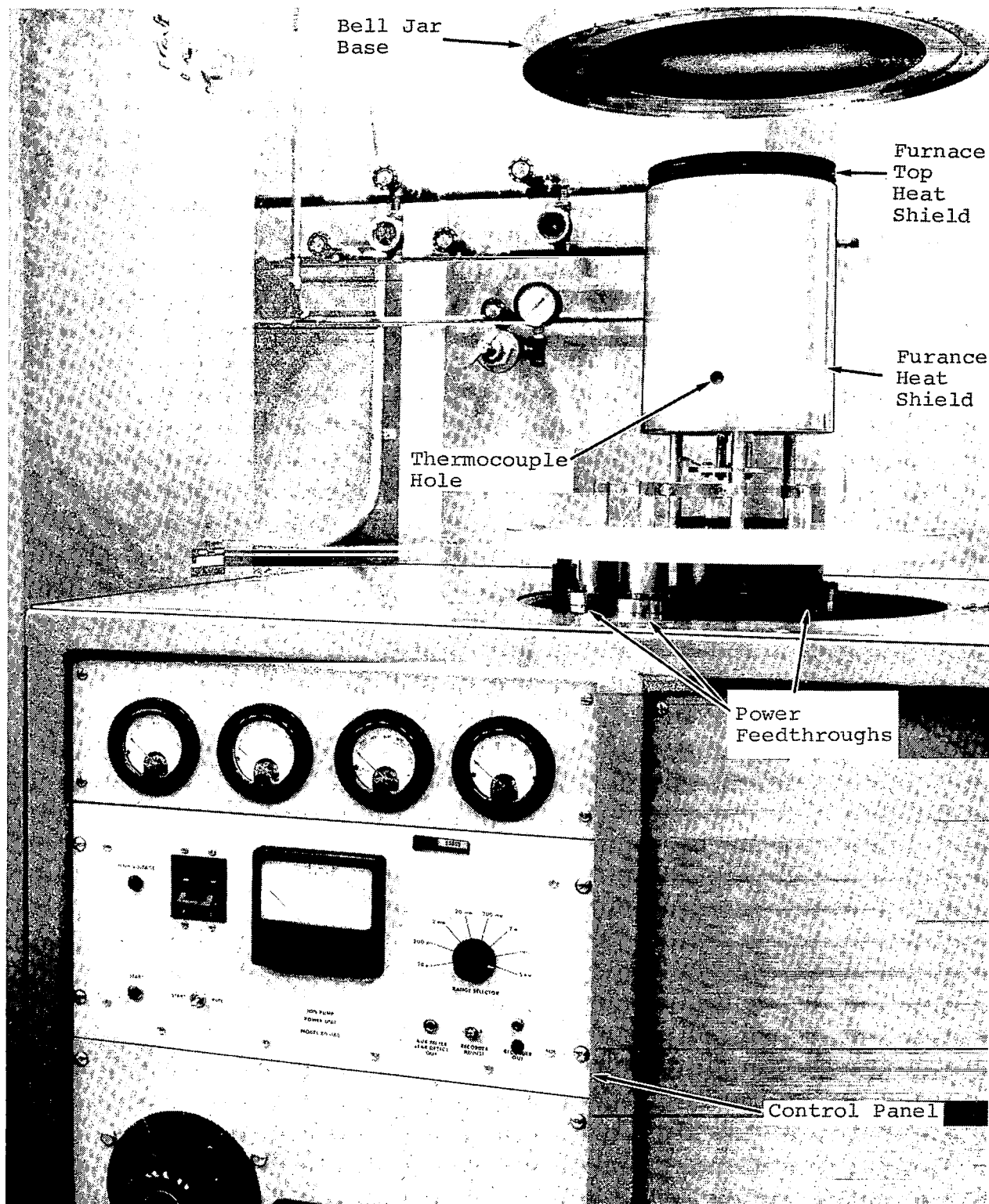


FIGURE II-9. Close up of Dual Vacuum Furnace Equipment

additional advantage of being able to discriminate between surface absorbed gas and bulk outgassing. The technique consisted of dropping the prepared sample into a precisely controlled, pre-conditioned vacuum furnace held at the test temperature. Selected m/e (mass-to-charge) ratios corresponding to the predominant gases and total pressure were monitored. The pumping rate of the system for each gas component was known so outgassing rates and total evolved gas volumes could be determined. As the test sample rapidly reached the furnace temperature, the outgassing curve exhibited three distinct pressure peaks corresponding to:

- a) Surface gases disturbed by sliding the sample into the furnace.
- b) Surface gas desorption from the sample.
- c) Diffusing gases from the bulk of the sample.

The leading edges and the tails of the pressure peaks overlap, but the peak maxima themselves are quite distinct. The third and last peak represented the bulk gases which were of greatest interest in this work. They were the gases which diffused out during operation of the bore seal and might introduce oxygen into the potassium vapor. The surface gases can be eliminated with proper system preparation.

The outgassing equipment shown in figure II-10 was utilized on the program with the following general procedure:

- a) A trial run was made to insure that the apparatus could be pumped down to a background level of less than  $2 \times 10^{-8}$  torr for all pertinent gases.
- b) The prepared specimen was inserted with a ferri-magnetic pusher into the horizontal part of the test chamber and the system was then sealed.
- c) The system was then pumped down, while baking the areas shown in figure II-11 until the total pressure was below  $10^{-6}$  torr, and partial pressure background was below  $2 \times 10^{-8}$  torr. The valving permitted pumping during bake-out at the full 40 l/sec capacity of the pump. However, during the outgassing run, a bypass valve was closed so that pumping took place through the 1 l/sec ( $N_2$ ) orifice.
- d) The furnace was heated to the desired ceramic outgassing temperature and again held until the desired base pressures were reached.

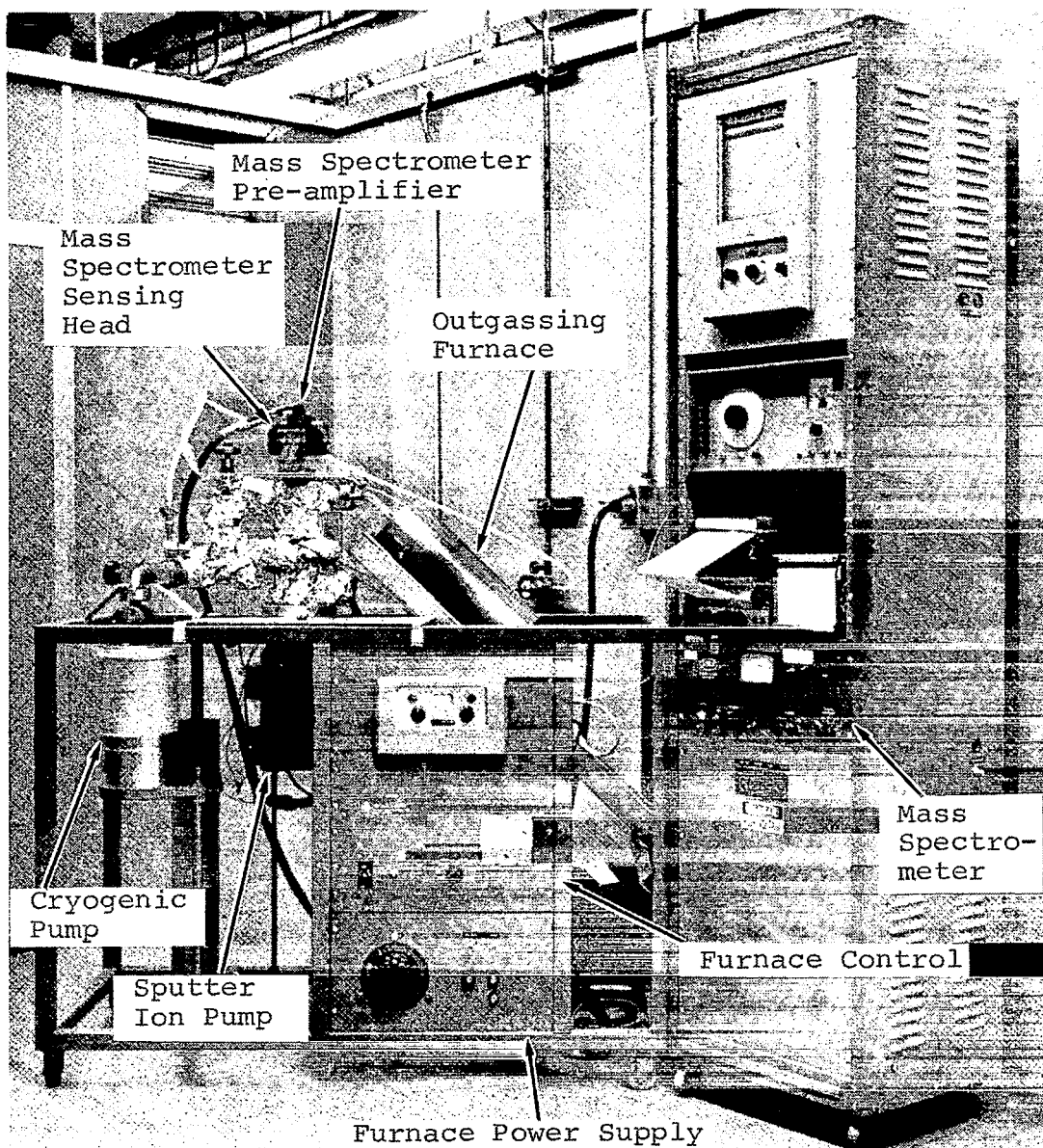


FIGURE II-10. Photograph of Ceramic Outgassing Analysis System

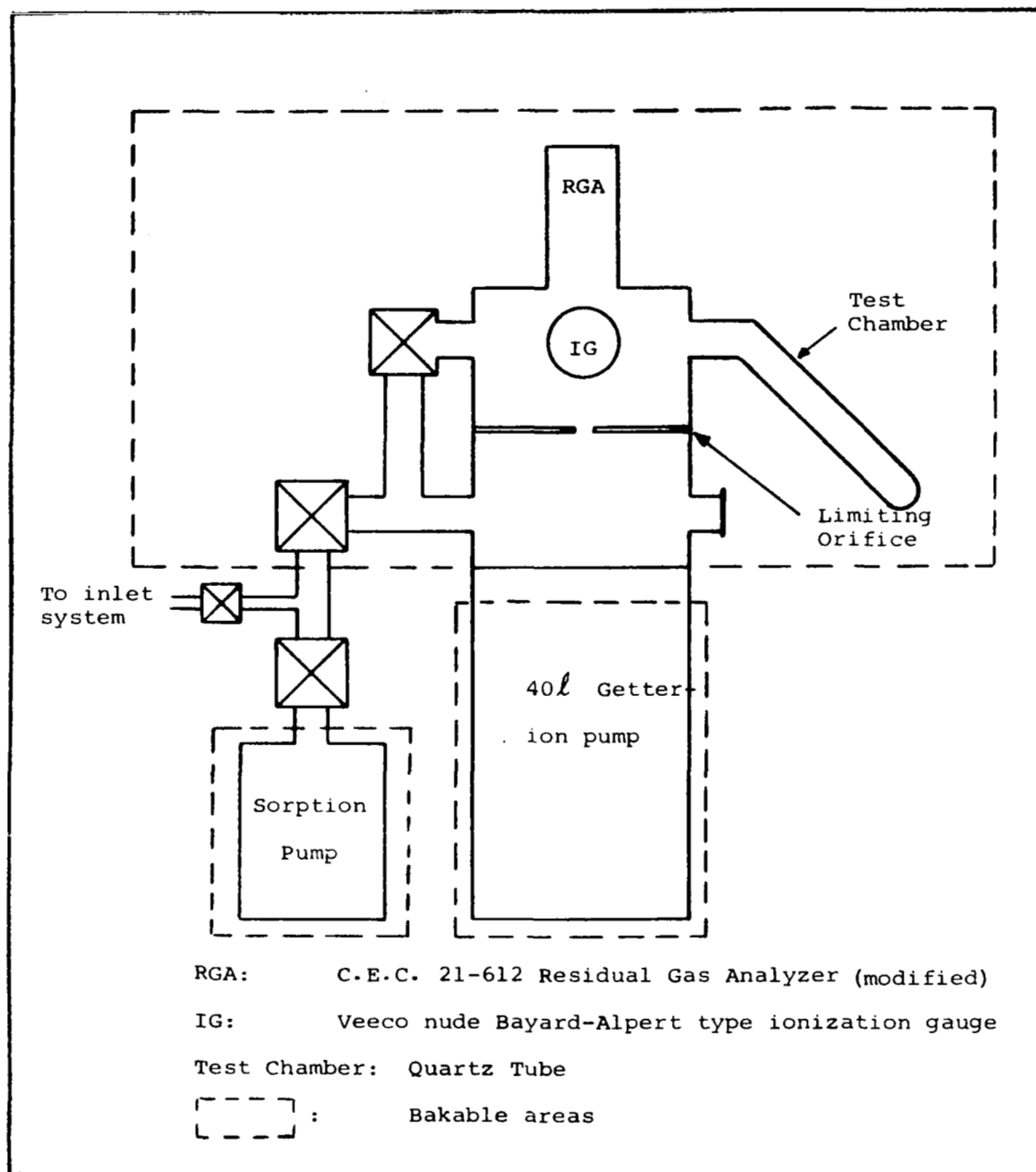


FIGURE II-11. Block Diagram of the Ceramic Outgassing Analysis System



- e) With the residual gas analyzer scanning masses 2 to 40 every second the specimen was pushed into the furnace with a magnet.
- f) After the partial pressures reach a nearly constant value (approximately 1 hour) the test was stopped.

#### 4. Ceramic-to-Metal Seal Testing Equipment

An Instron Tensile Test Machine was used for measuring the modulus-of-rupture (MOR) of brazed ceramic-to-metal MOR specimens. The specimens, jigs, and methods were described previously (ref. II-1). The testing of tab peel strength and ceramic-to-metal vacuum integrity specimens were also described in the same report.

New and more advanced tests were applied during this program. These included elevated temperature modulus-of-rupture and vacuum-leak tests on ceramic-to-metal seals. In addition vibration, thermal shock, and thermal cycling tests were performed. The new equipment and procedures are described in the following sub-sections.

##### a. ELEVATED TEMPERATURE FLEXURAL STRENGTH APPARATUS

An apparatus (figure II-12) was constructed in which the standard four-point loading modulus-of-rupture test could be performed on brazed ceramic-to-metal specimens at elevated temperatures. The apparatus was mounted in the Instron Tensile Test Machine and measurements were made in the same manner as at room temperature. The following procedures were followed in making the elevated temperature tests.

- 1) The apparatus was positioned in the Instron machine with a specimen in place on the anvils.
- 2) The apparatus was evacuated and purged slowly with argon when the pressure reached 200 torr.
- 3) The chamber was backfilled with high-purity argon.
- 4) The furnace was then heated to 600° F.
- 5) The furnace was then evacuated and outgassed until the pressure reached 1 torr.
- 6) The chamber was again backfilled with high-purity argon and the temperature raised to the desired level.

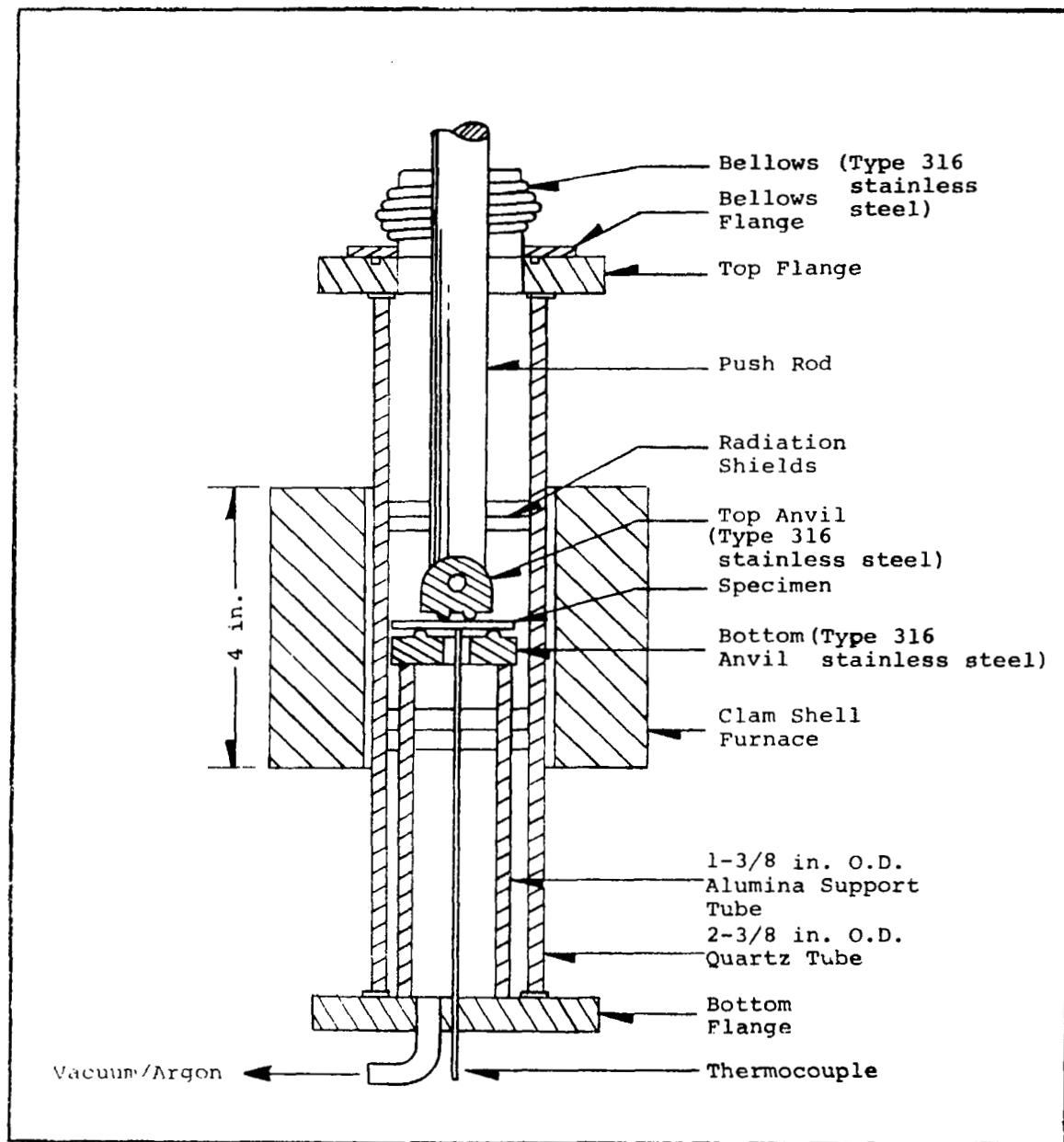


FIGURE II-12. Schematic of Elevated Temperature Modulus of Rupture Test Apparatus

- 7) The argon pressure was adjusted to one atmosphere and the modulus-of-rupture bar was tested at a strain rate of 0.1-inch per minute while recording the force on an x-y recorder.
- 8) Finally the furnace was removed from the apparatus to permit rapid cooling.

A normal test at 1600° F was completed in approximately three hours. Trial tests on Thermalox 998<sup>4</sup> modulus-of-rupture bars at 1400° and 1600° F resulted in flexural strength values nearly the same as previously found in the normal room temperature flexural strength tests. This was in general agreement with results reported in the literature (see Appendix C).

#### b. VIBRATION TEST APPARATUS

A vibration test fixture (figure II-13) was made from 6061 aluminum alloy to hold a 2-inch diameter by 2-inch long ceramic-to-metal vibration test assembly. The fixture was mounted on an Alidyne Al74 shaker table and a test was conducted as follows:

- 1) The assembly was leak checked.
- 2) The assembly was then mounted in the vibration fixture with strain gages mounted as shown in figure II-14.
- 3) The assembly was vibrated axially at 10 g's, with a rapid scan from 0 to 2000 cycles per second to locate the resonance frequencies.
- 4) The scan was repeated with a five minute hold at each resonance frequency.
- 5) The scan was then repeated after removing the test assembly to obtain the resonance points of the shaker and vibration jig.
- 6) The assembly was vacuum-leak checked again after the test was completed.

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<sup>4</sup>Trade name for the 99.8% BeO product of the Brush Beryllium Company, Elmore, Ohio.

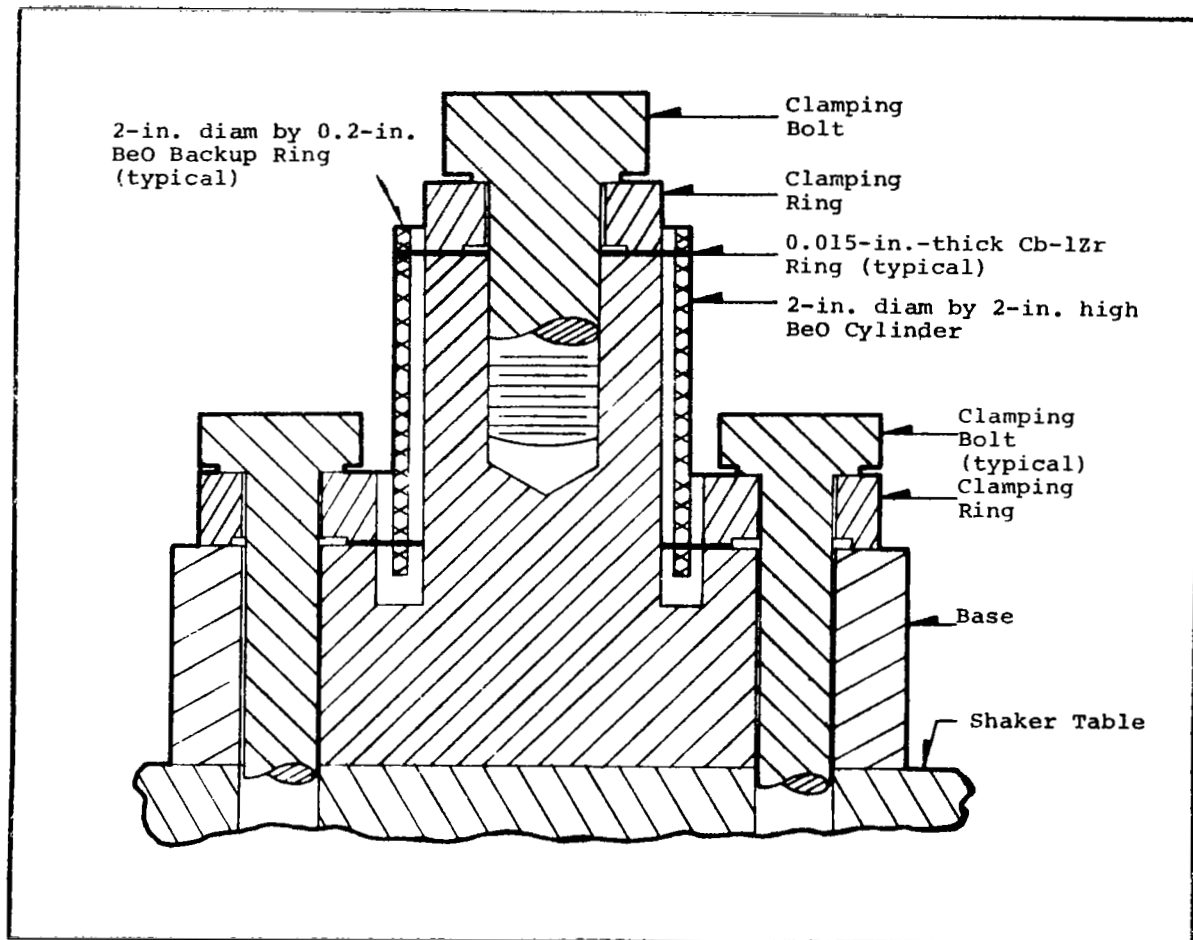


FIGURE II-13. Schematic of Two-Inch Diameter by Two-Inch High Bore Seal Vibration Assembly Mounted in Vibration Fixture

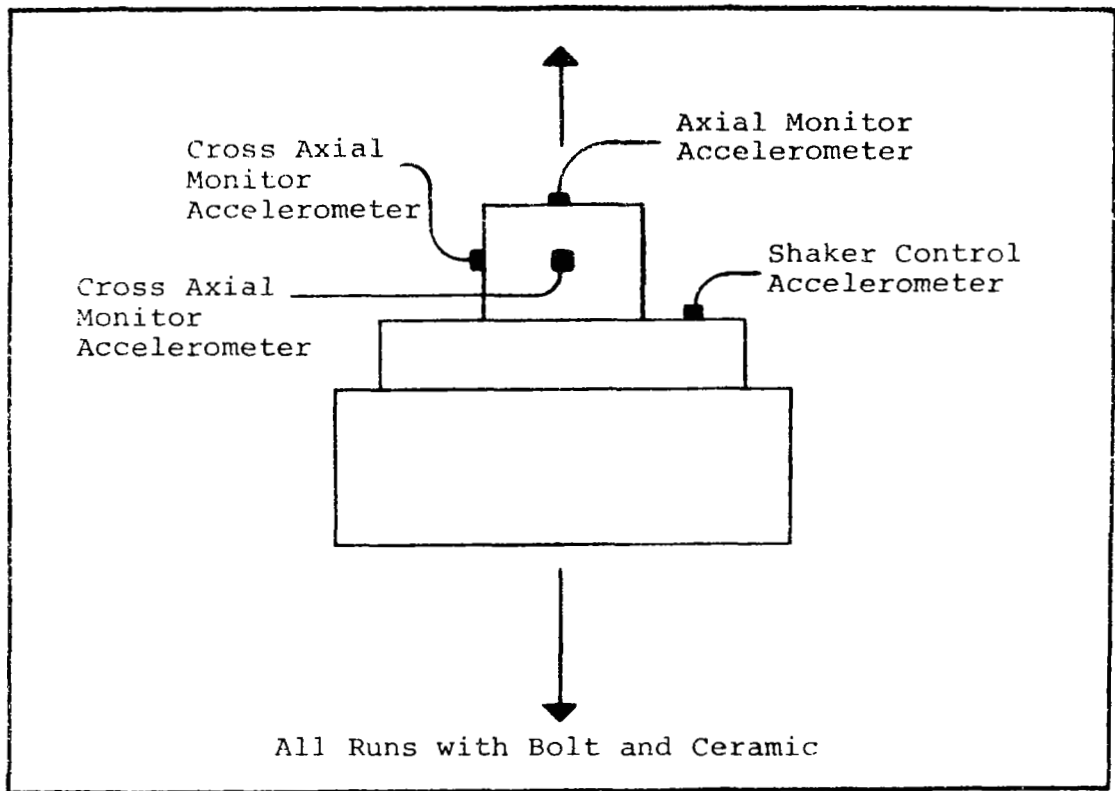


FIGURE II-14. Schematic Showing the Location of Strain Gauges on Ceramic Tube and Metal End-Member, on the Two-Inch Diameter Bore Seal Assembly Before Vibration Testing

c. ELEVATED TEMPERATURE VACUUM-LEAK TEST AND THERMAL CYCLING AND THERMAL SHOCK APPARATUS

The brazing furnace was modified (figure II-15) to conduct high-temperature vacuum-leak checks and thermal-cycle and thermal-shock tests on 2-inch diameter by 2-inch long model bore seals (Section II.C.7). A helium supply and specimen mounting tube were added so that a helium pressurized specimen could be mounted in the hot zone.

The elevated temperature vacuum leak check and thermal cycle test was conducted as follows:

- 1) The test assembly was mounted in the susceptor and evacuated. All joints were leak checked.

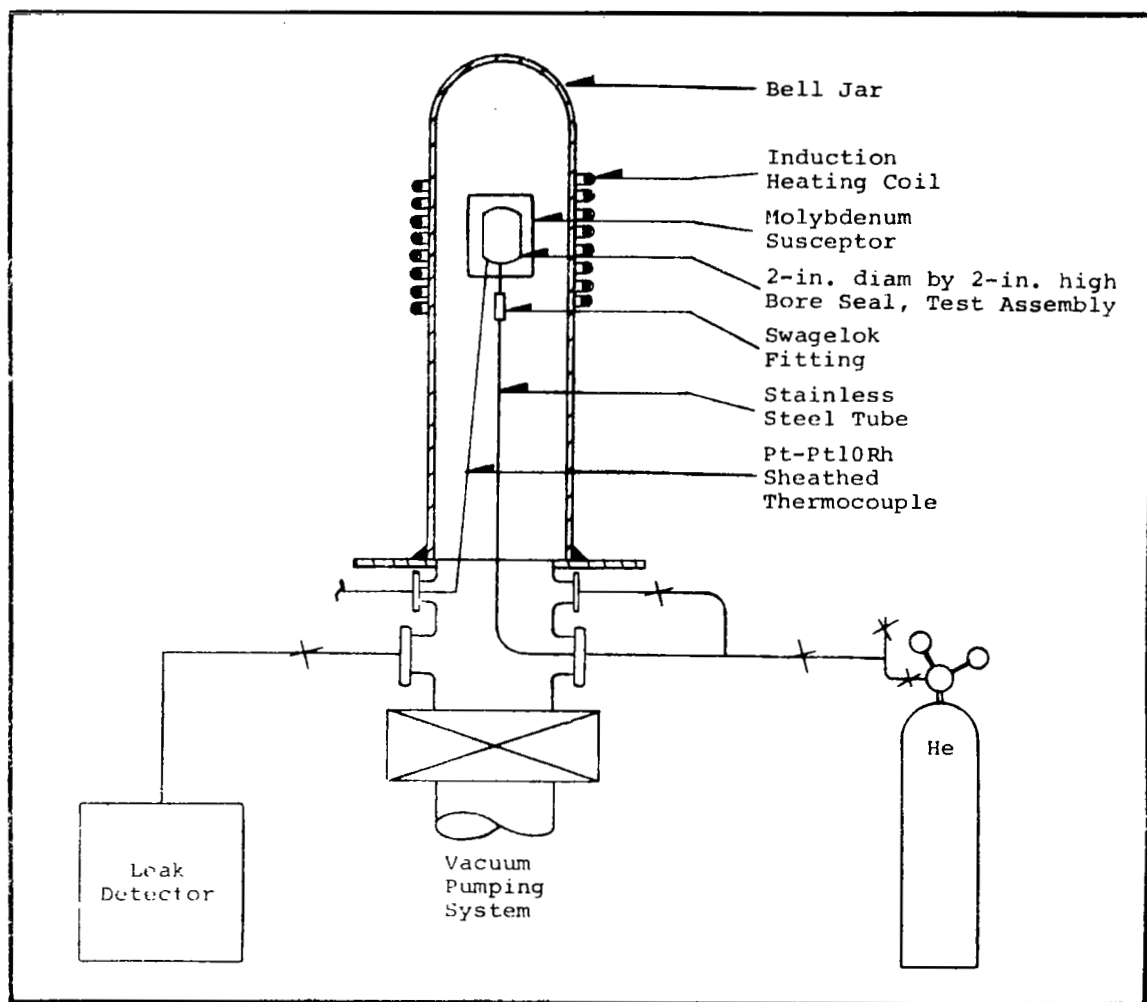


FIGURE II-15. Schematic of Hot Leak Check and Thermal Cycling Apparatus

- 2) The bell jar was installed and both sides of test assembly were evacuated.
- 3) The leak rate was measured with a trace of helium inside the assembly, then with 2-1/2, 5, 7-1/2, and 10 psia helium inside the bore seal.
- 4) The assembly was evacuated and heated to 1400° F at the rate of 25° F per minute.
- 5) Step No. 3 was then repeated.
- 6) The apparatus was then cooled to less than 350° F at a rate of approximately 25° F per minute.
- 7) Step No. 3 was repeated once again.
- 8) Steps 4 to 6 were repeated as required. See Section II.C.7. for the actual number of cycles and results of the test on this program.

The thermal shock test was conducted in the same manner as noted above except for the heating and cooling rates which were 100° F per minute.

## C. CERAMIC-TO-METAL SEALS

### 1. Analysis and Selection of Sealing Materials and Systems

#### a. BORE SEAL MATERIALS

Columbium-1% zirconium alloy was used both as a capsule material and as a metal member in the ceramic-to-metal test assemblies on this program and on NASA contract NAS3-4162. The oxygen level of all refractory metals used was below 300 ppm. Reliable, vacuum-tight, potassium-resistant welds were made by either tungsten inert-gas or electron-beam welding techniques. Test capsules for this program were welded by the electron-beam welding method. Metallurgical cross-sections of joints annealed at 2200° F for one hour and subsequently life tested showed good joint integrity. Reliable ceramic-to-metal seals were fabricated with columbium-1% zirconium, D-43 columbium alloy (Cb-10W-1Zr-0.1C) and T-111 tantalum alloy (Ta-8W-2Hf) were also satisfactory for the fabrication of ceramic-to-metal seals (ref. II-1).

High-purity alumina and beryllia ceramics were selected previously on the basis of their thermodynamic stability. Sapphire<sup>5</sup>, Lucalox<sup>6</sup>, and Thermalox 998<sup>7</sup> were found to retain their intrinsic strength and resist attack by potassium during 500-hour exposure tests at 1600° F (ref. II-1). Since actual bore-seal ceramics are required to operate for long periods, 2000-hour alkali-metal exposure tests were carried out on this program.

Additional ceramic bodies were tested for use in the event that the above materials prove unsatisfactory. High-purity yttria<sup>8</sup> and Thermalox 998<sup>7</sup> beryllia, both manufactured to limit the content of SiO<sub>2</sub> and other thermodynamically unstable species, were ordered in the forms of modulus-of-rupture bars and small cylinders.

This section describes the search for a method of joining columbium-1% zirconium to a ceramic which will result in a system resistant to alkali metal for longer periods of exposure.

#### b. CERAMIC-TO-METAL JOINING

Two joining techniques were emphasized on this program: active metal brazing, and brazing to metallized ceramics. The active brazing technique was found to be more promising on the previous program (ref. II-1) and most of the effort on this program was devoted to it. The principles underlying the process and factors considered in selecting the most promising systems are outlined here.

Most metals do not wet ceramics. Metals possessing high free energies of oxide formation ( $-\Delta F_f$ ) as a class can wet and join ceramics to other metals.

"Active metals" are those that react according to  $M + CeO_x \rightarrow MO_x + Ce$ , where M = metal and Ce = ceramic. The metals titanium, columbium, zirconium, hafnium, yttrium and vanadium are all very active metals with high melting temperatures. These metals may be alloyed with each other and with other metals (such as nickel, copper, beryllium, and silver) in order to reduce their reactivities with the ceramic and metal members, and to lower

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<sup>5</sup>Single crystal alumina (~100% Al<sub>2</sub>O<sub>3</sub>) supplied by Linde Division, Union Carbide Corporation.

<sup>6</sup>Trade name for the 99.8% Al<sub>2</sub>O<sub>3</sub> product of the General Electric Company, Lamp Division, Cleveland, Ohio.

<sup>7</sup>Trade name for the 99.8% BeO product of the Brush Beryllium Company, Elmore, Ohio.

<sup>8</sup>Supplied by Coors Porcelain Company, Golden, Colorado.



their brazing temperatures. Lower brazing temperature is conducive to avoiding warpage of large structures.

The essential requirements for joint stability which must be met by any sealing system for this program were:

- 1) Resistance of the metal, the ceramic, the brazing alloy, and the reaction products formed at the interfaces during brazing to potassium vapor and liquid at 1600° F.
- 2) Intrinsic stability in a vacuum of  $1 \times 10^{-9}$  torr at 1600° F.
- 3) High brazed strength. This is promoted by a ductile matrix and a ductile layer next to the ceramic.

Although empirical rules can act as a guide, no theory is available which will predict the actual resistance of metals to potassium (refs. II-6 and II-7). In general, the refractory metals, from groups IV, V, and VI, of the periodic table, include the most suitable corrosion resistant materials. However, other materials, if combined in the form of stable intermetallics, (e.g.,  $\text{CbBe}_2$ ) offer promise. It would be expected that the more refractory the intermetallic, the more resistant it would be to corrosion. For example,  $\text{CbBe}_2$  (MP = 3812° F) would be superior to  $\text{CbBe}_{12}$  (MP = 3002° F).

The atomic radii of the elements, table II-1, can aid in predicting solid solubility. According to the Hume-Rothery rules, if less than a 15 percent difference in radii exists, complete solid solubility will be possible. However, this rule is of no help with regard to predicting kinetics, i.e., their liquid solubility rates in alkali metals.

In general, the higher the melting point of the metal and the lower the melting point of the alkali metal, the less will be the liquid solubility. One can readily see that lithium may enter the refractory metal lattice by the solid solution processes, thus its mode of attack on oxygen present in the alloy can be through the crystal lattice, as well as along its grain boundaries.

The oxygen level of a brazing alloy must be low in order that an alkali metal will not react with the oxygen and leave a porous and thereby weakened metal. This criterion is not as critical if the oxygen is tied up by a getter-metal alloy addition in the form of very stable

TABLE II-1. Atomic Radii and Melting Points of Braze Alloy Constituents Compared to the Alkali Metals

Element	Melting Point (a)		Atomic Radii (b) (Angstrom units-Å)
	(°F)	(°C)	
Yttrium	2748	1509	1.80
Zirconium	3366	1852	1.60
Columbium	4474±18	2468±10	1.46
Titanium	3035±18	1668±10	1.47
Molybdenum	4730	2610	1.39
Tungsten	6170	3410	1.39
Vanadium	3450±50	1900±25	1.34
Beryllium	2332	1277	1.12
Cesium	83.6	28.7	2.67
Potassium	146.7	63.7	2.35
Sodium	208.1	97.8	1.90
Lithium	357	180.5	1.55
(a) Metals Handbook, 8th Edition, 1961			
(b) Hume-Rothery, W., The Structure of Metals and Alloys. The Institute of Metals, London, 1947. Complete solid solubility will be possible if less than 15 percent difference in radii exists.			

oxides such as  $ZrO_2$ ,  $Y_2O_3$ , or  $BeO$ . In this case, the braze will be stable until all of the getter-metal has reacted.

The conditions for the elevated temperature stability in vacuum must be considered independently. Under some test conditions gaseous oxygen and nitrogen will be present on the side of the braze exposed to vacuum. It is important to choose brazing alloys which exhibit a low diffusion rate with respect to oxygen and which have built-in getters to absorb the oxygen and nitrogen. Some alloys do not tie up the oxygen unless they have been annealed at high temperatures as is done in the post-weld annealing of columbium-1% zirconium.

The ideal mechanical condition for a ceramic-to-metal brazed joint is that it be ductile, with adequate strength to resist stresses imposed on it. Ceramics are brittle; therefore, a hard brittle phase (e.g., an intermetallic) next to the ceramic is undesirable. An ideal situation is for any hard phase in the braze to be of small crystal size and to be surrounded by a ductile matrix phase. A laminar phase separation system should be avoided.

Different ceramic substrates can introduce different phase distributions. In the case of the 75Zr-19Cb-6Be brazing alloy, a solid solution was noted immediately adjacent to the beryllia substrate, but in the case of an alumina substrate, a harder aluminum-containing solid solution phase was noted. The former case is illustrated in figure II-20. Phase changes may be expected to occur in brazing alloys maintained at 1600° F and above. The precipitation or growth of hard, non-ductile phases is undesirable if mechanical joint integrity is to be maintained.

One of the considerations in the selection of brazing alloys is the melting temperature. Phase diagrams for many binary metal systems of interest on this program are available. The lowest temperature in each listed system is shown in table II-2.

Since promising candidate brazing alloys having melting temperatures below 2600° F were available, binary systems with melting temperatures higher than this received limited attention as brazing alloys by themselves. (Alloys having ~2500° F brazing temperatures were expected to provide candidates with adequate strength and corrosion resistance at 1600° F and still avoid warpage of the future relatively large-diameter, thin-wall ceramic

TABLE II-2. Phase Relations in Selected Binary System of Interest for Brazing Alloys

Binary System	Lowest Melt		Phase Composition	Remarks
	Temperature (°C)	Solute (weight percent)		
Be-Cb	1260	5	CbBe <sub>12</sub> -Be	Eutectic
Cb-Mo	2468 (Cb)	-	Cb-Mo	Continuous Solid Solubility
Cb-Ti	1720	-	Ti	Pure Ti $\beta \rightarrow \alpha$ (870°C - 500°C)
Cb-Cl	1435	8	Cb-Th	Simple Eutectic
Cb-Cr	1810	35	Cb-V	$\beta$ -solid solution (s.s.)
Cb-W	2468 (Cb)	-	Cb-W	Continuous Solid Solubility
Y-Cl	1470	6	Cb-Y	Eutectic
Zr-Cb	1800	30	Cb-Zr	$\beta$ -s.s., eutectoid (below 1000°C)
Ti-Be	950	4-10	Ti-Be <sub>3</sub> Ti <sub>4</sub>	Eutectic
Ti-Mo	1668 (Ti)	-	Ti-Mo	Continuous Solid Solubility with $\alpha$ -Ti
Th-Ti	1130	12.5	Th-Ti	Eutectic
Ti-V	1620	30	Ti-V	$\beta$ -s.s. $\rightarrow \alpha$ (887°C - )
Ti-W	1668 (Ti)	-	Zr-Ti	Peritectic (1880°C - 52% W)
Y-Ti	1385	12	Ti-Y	Eutectic $\beta \rightarrow \alpha$ (870°C)
Ti-Zr	1600	50	Ti-Zr	$\beta$ -s.s. $\rightarrow \alpha$ (870°C - 500°C)
Zr-Be	976	6	Zr-ZrBe <sub>2</sub>	Eutectic, ZrBe <sub>2</sub> peritectic
Zr-Mo	1520	31	Zr-ZrMo <sub>2</sub>	Eutectic, ZrMo <sub>2</sub> peritectic
Th-Zr	1350	46	Zr-Th	Minimum
Zr-V	1230	30	Zr-ZrV <sub>2</sub>	Eutectic, ZrV <sub>2</sub> peritectic
W-Zr	1630	20	Zr-ZrW <sub>2</sub>	Eutectic, ZrW <sub>2</sub> peritectic
Y-Zr	1385	44	Zr-Y	Eutectic
V-Be	1600	15	V-VBe <sub>2</sub>	Eutectic
V-Mo	1240	-	V-Mo	Continuous Solid Solubility
Th-V	1430	15	V-Th	Eutectic
V-W	1630	20	V-W	Eutectic
Y-V	1455	7	V-Y	Simple eutectic
Y-Be	1070	6	Y-YBe <sub>13</sub>	Eutectic; YBe <sub>13</sub> (M.P. 1920°C)
Y-Hf	1425	13	Y-Hf	Eutectic

cylinder.) Those binaries with melting temperatures lower than 2500° F are Cb-Be, Ti-Be, Ti-Th, Ti-Y, Zr-Be, Zr-V, Zr-Y, and Y-Be. Most of these can be rejected on the basis of objectionable properties reported in this section.

Cb-Be forms the Cb-Be<sub>12</sub> compound on solidification. This intermetallic compound was noted previously as being relatively unstable. It probably would not be reactive enough to bond to the ceramic.

Ti-Be and Zr-Be:

The binaries are probably too reactive with the ceramic, their intermetallic compounds are relatively unstable, and the brazement would probably have lower creep and yield strength than ternaries of interest.

Ti-Th, Ti-Y, Zr-Y:

These binaries are probably highly reactive.

Zr-V:

Intermetallic compounds present are relatively unstable, but the binary is a possible candidate.

Y-Be:

This is considered to be a promising binary candidate.

Several binaries that are partially liquid in the 2550° F range may also be possible candidates. Of these, Cb-Y appeared to be the most promising.

Although none of the binary alloys appeared to have properties as desirable as the tested ternary alloys, their phase diagrams and characteristics are of interest as an aid in estimating the properties of untested ternaries. The ternary phase diagrams with the desirable combination of elements are not complete enough to predict exact behavior. When combined with a fourth element (e.g., with partial dissolution of the metal member during brazing) the evaluation is even more complex. However, the approximate behavior of new ternary alloys can be estimated from the available data and the appropriate binary diagrams.

Appreciable lowering of the melting point cannot be expected by combining binary compositions showing complete solid solution. However, by combining an eutectic with a solid solution series or with another eutectic, a

further lowering of the melting point may be expected to occur.

Based on corrosion resistance, vacuum integrity, and strength, the following alloys were considered to be the prime candidates from the previous program:

75Zr-19Cb-6Be - with  $\text{Al}_2\text{O}_3$  or BeO

48Zr-48Ti-4Be - with  $\text{Al}_2\text{O}_3$  or BeO

56Zr-28V-16Ti - with BeO

Other brazing alloys were selected from those (see table II-3) evaluated on the previous program<sup>9</sup>. The alloys marked in table II-3 were chosen for further consideration.

In addition to these alloys, the following new brazing alloys were selected for evaluation:

<u>Alloy</u>	<u>Melting Temperature</u>
Y-6Cb	2680° F
Y-6Be	1970° F
Y-46Zr	2530° F

The active metal brazed joint interface is the focus of attack by potassium if thermodynamically unstable oxides are present. Therefore, it is desirable to have systems that result in the most stable oxide reaction products. Oxides of yttrium and zirconium, which are expected to form while brazing ceramic to metal with the alloys just listed, are such thermodynamically stable oxides (ref. II-1).

During the course of this program, the potential beneficial effects of evaporated metallizing layers and chemical vapor deposition of diffusion barrier layers became apparent. Active-metal alloy brazing tests and evaluation of these processing techniques are described in the following section.

## 2. Development and Testing of Selected Ceramic-to-Metal Sealing Systems

The systems included among those selected for evaluation were changed during the program as new data were obtained and evaluated.

<sup>9</sup>Contract NAS3-4162

TABLE II-3. Active Metal Brazing Alloys Selected for Further Study From Previous Program<sup>(a)</sup>  
(With Experimental Brazing Temperatures)  
for Cb-1Zr to 99.8% BeO Bonding

Nominal Alloy (weight percent)	Brazing Schedule <sup>(b)</sup>			
	10 min. hold temp. <sup>(c)</sup>		Brazing temperature	
	(°F)	(°C)	(°F)	(°C)
75Zr-19Cb-6Be <sup>(d)</sup>	1805	985	1985	1085
68Ti-28V-4Be <sup>(e)</sup>	1832	1000	2372	1300
56Zr-28V-16Ti <sup>(d)</sup>	2102	1150	2372	1300
48Ti-48Zr-4Be <sup>(d)</sup>	1742	950	2030	1110
46Ti-46Zr-4Be-4V <sup>(e)</sup>	1652	900	1832	1000
50Zr-30V-20Cb <sup>(e)</sup>	2102	1150	2516	1380
65V-35Cb	-	-	3398	1870
70Ti-30V	-	-	3002	1650
60Zr-25V-15Cb <sup>(e)</sup>	2192	1200	2436	1330
50Zr-30Ti-20V <sup>(e)</sup>	2282	1250	2732	1500
40Zr-30Ti-30V		-	2336	1280
35Ti-35V-30Zr <sup>(e)</sup>	2282	1250	2804	1540
50Ti-30Zr-20V		-	2597	1425
62Ti-30V-8Si	2192	1200	2480	1360

(a) Contract NAS3-4162

(b) Revised January 1966 to the current schedules. Actual brazing temperatures reported in text may differ. (See table II-4.)

(c) Active metal brazing is done by raising the vacuum furnace temperature gradually to the temperature shown in the left column for a specific alloy. The pressure in the furnace is maintained at  $10^{-5}$  torr or less during the cycle. This temperature is held for ten minutes, then raised rapidly to the brazing temperature shown. The power is turned off after five minutes at the brazing temperature.

(d) Alloys considered to be prime candidates for long term applications.

(e) Alloys selected for further evaluation.

Presentation of the development effort in a chronological order was considered to be less informative than that presented on a system basis; therefore, the discussion in this section is outlined on a system basis. However, to update the reader on the development program, a brief historical summary will be presented first.

The systems listed in Section II.C.1.b. were selected for evaluation on the basis of test results obtained on the previous bore seal program<sup>10</sup> (ref. II-1). Ceramic-to-metal joining tests were conducted with a number of the brazing alloys listed in table II-3. Columbium-1% zirconium was selected as the metal member. Thermalox 998<sup>11</sup> beryllia (99.8% BeO), Ei-3W<sup>12</sup> alumina (99.7% Al<sub>2</sub>O<sub>3</sub>), Lucalox<sup>13</sup> (99.8% Al<sub>2</sub>O<sub>3</sub>), and sapphire<sup>14</sup> (~100% Al<sub>2</sub>O<sub>3</sub>) were tested in alkali metals singly and after brazing to metals. Beryllia emerged as the best ceramic candidate available in the sizes required for potential bore seals.

On this program, wire and sheet form of brazing alloys were processed and tested, but these new forms were not adopted and were not determining factors in the final brazing alloy selection. Additional brazing tests were made on the following systems which emerged as candidates from the 500-hour, 1600° F potassium exposure test. Ei-3 alumina (48Ti-48Zr-4Be) Cb-1Zr; BeO (56Ti-28V-16Zr) Cb-1Zr; and Ei3W alumina (75Zr-19Cb-6Be) Cb-1Zr. Also as a result of wetting layer tests, 60Zr-25V-15Cb emerged as a strong candidate when brazed to Cb-1Zr and Thermalox 998 beryllia that had been coated with a wetting layer of evaporated molybdenum.

Low-silica Thermalox 998 and yttrium oxide were obtained as alternate ceramics. After the first potassium exposure test on this program, the low-silica Thermalox 998 (99.8% BeO) emerged as the leading ceramic candidate.

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<sup>10</sup> Contract NAS3-4162

<sup>11</sup> Trade name for the 99.8% BeO product of the Brush Beryllium Company, Elmore, Ohio

<sup>12</sup> Trade name for high-purity alumina (99.7% Al<sub>2</sub>O<sub>3</sub>) product of the Western Gold and Platinum Co., Belmont, California.

<sup>13</sup> Trade name for the 99.8% Al<sub>2</sub>O<sub>3</sub> product of the General Electric Company, Lamp Division, Cleveland, Ohio.

<sup>14</sup> Single crystal ~100% Al<sub>2</sub>O<sub>3</sub> obtained from the Linde Division, Union Carbide Corporation.



Finally, the molybdenum-metallized low-silica Thermalox 998 brazed to Cb-1Zr with 60Zr-25V-15Cb emerged as the potentially best combination, followed by low-silica Thermalox 998 brazed with the alloy 56Ti-28V-16Zr. Four-inch model bore seals were constructed from the first combination (Section II.C.8). Both combinations were used to construct two-inch diameter model bore seals for elevated temperature vacuum integrity and thermal shock tests, (Section II.C.7) and for extended potassium exposure tests.

In this section, the development and analysis of the principal selected systems will be discussed.

- 48Ti-48Zr-4Be - with Ei-3W alumina
- 75Zr-19Cb-6Be - with Ei-3W alumina
- 56Ti-28V-16Zr - with low-silica Thermalox 998
- 60Zr-25V-15Cb - with low-silica Thermalox 998

Development work with other combinations will follow.

#### a. METHODS OF TESTING

##### (1) Modulus-of-Rupture (Flexural) Strength and Tab Peel Strength

Various methods were utilized in the evaluation of specimens in seal development. The principal basis for mechanical evaluation of ceramics was the modulus-of-rupture (flexural) strength using 0.1-inch square by 1.1-inch long modulus-of-rupture bars in a four-point loading. The principal mechanical means of evaluating joining systems were by measuring flexural strength and tab-peel strength of modulus-of-rupture and tab-peel (TP) assemblies, respectively. The modulus-of-rupture assembly consisted of two ceramic modulus-of-rupture bars which had been brazed end-to-end with a shim of 10-mil-thick Cb-1Zr alloy between the ceramics. The tab-peel assembly consisted of a 5-mil-thick by 0.1-inch-wide by 1.5-inch-long strip of Cb-1Zr alloy brazed to the side of a ceramic modulus-of-rupture bar. Details of the tests and assemblies were described in an earlier Bore Seal Report (ref. II-1), but the assemblies are shown for convenience in figure II-16.

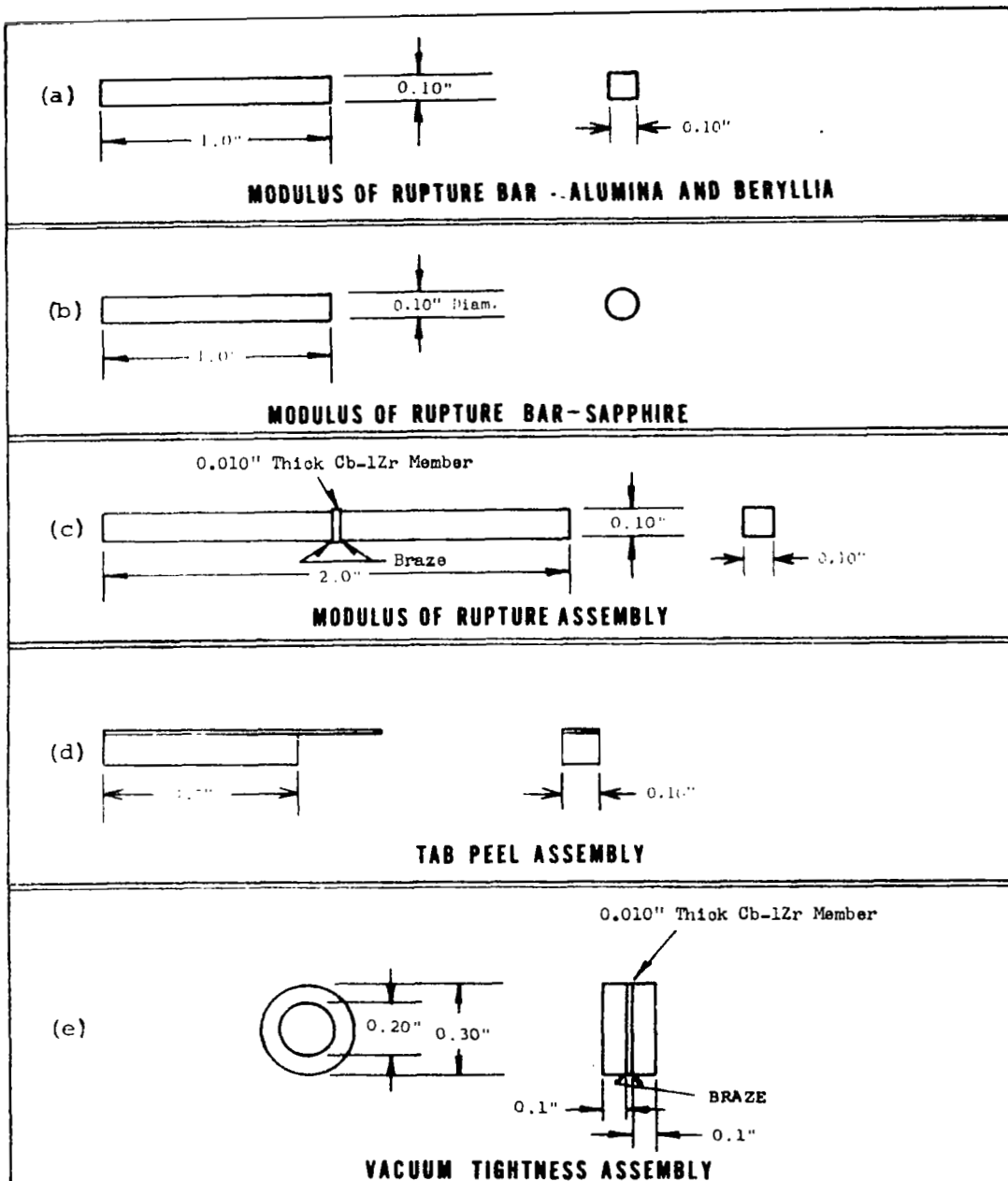


FIGURE II-16. Ceramic-Metal Seal Test Assembly Geometries

## (2) Vacuum Integrity Test

Vacuum tightness is as important as the strength in a bore seal. Many brazements were found to retain full strength even though they were not vacuum tight. A sandwich type vacuum tightness (VT) assembly consisted of a 0.5-inch-diameter disk of Cb-12r alloy 10-mil thick brazed between two ceramic washers. Thermalox 998 washers were 0.4-inch outside diameter by 0.3-inch inside diameter by 0.1-inch thick. Lucalox<sup>15</sup> washers were 0.375-inch outside diameter by 0.285-inch inside diameter by 0.1-inch thick. Two of either type assembly were brazed with nearly every group of brazed modulus-of-rupture bars. Each assembly provided for two vacuum tightness tests.

## (3) Brazing Tests

Standard brazing conditions were retained from previous work, and were initially used for various alloys. Many tests were conducted with modulus-of-rupture, tab peel, and vacuum tight assemblies to determine whether optimum time-temperature conditions were being used. As a result of these tests, adjustments in the standard conditions were made, and, in some cases, it was found that good seals could be made under a wide range of brazing conditions. Table II-4 describes the various brazing alloys and conditions used on this program.

## (4) Metallography, Microhardness, and Electron Microprobe Analysis

Analyses of the microstructures of brazing combinations were carried out on sections of selected vacuum-tight specimens. Electron microprobe analyses were performed by a contract source<sup>16</sup>.

## (5) Alkali Metal and Vacuum Exposure at Elevated Temperature

Final evaluation of different sealing systems was performed by determining the effects of alkali metal exposure, based on the previously listed tests. Experimental details of the exposure tests are given in Section II.C.6.

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<sup>15</sup>Trade name for the 99.8% Al<sub>2</sub>O<sub>3</sub> product of the General Electric Company, Lamp Division, Cleveland, Ohio.

<sup>16</sup>Materials Analysis Company, Palo Alto, California.

TABLE II-4. Brazing Alloy Ceramics and Conditions Investigated on this Program (The metal member in all cases was Cb-1Zr)

Brazing Alloy	Ceramic	Brazing Conditions							
		Temp. (°F)	Time (min)	Temp. (°F)	Time (min)	Temp. (°F)	Time (min)	Temp. (°F)	Time (min)
56Ti-28V-16Ti	BeO (a)	2372	5						
	BeO (a)	2376	0	2376	5	2376	30	2436	5
	Al <sub>2</sub> O <sub>3</sub> (b)	2376	0	2376	5	2376	30	2436	5
	Al <sub>2</sub> O <sub>3</sub> (b)	2273	0	2273	5	2453	5		
70Zr-10Cb-6Be	BeO (a)	1985	5						
	Al <sub>2</sub> O <sub>3</sub> (b) (c)	1985	5						
46Zr-48Ti-4Be	BeO (a)	2030	5						
	BeO (a)	1940	0	1940	5	1940	30	2120	5
	Al <sub>2</sub> O <sub>3</sub> (b)	1940	0	1940	5	1940	30	2120	5
Y	Al <sub>2</sub> O <sub>3</sub> (c)	2552	5						
	BeO (a)	2552	5						
Y-6Be	Al <sub>2</sub> O <sub>3</sub> (c)	2552	5						
	BeO (a)	2552	5						
Y-46Zr	Al <sub>2</sub> O <sub>3</sub> (c)	2552	5						
68Ti-28V-4Be	BeO (a)	2372	5						
46Ti-46Zr-4Be-4V	BeO (a)	1832	5						
60Zr-25V-15Cb	BeO (a)	2328	5	2436	5	2526	5	2616	5
50Zr-30V-20Cb	BeO (a)	2515	5	2732	10				
35Ti-35V-30Zr	BeO (a)	2804	1						
50Zr-30Ti-20V	BeO (a)	2732	10						
(a) BeO was Thermalox 998 (99.8% BeO) Product of Brush Beryllium Co., Elmore, Ohio. (b) Al <sub>2</sub> O <sub>3</sub> was Li-3W (99.7% Al <sub>2</sub> O <sub>3</sub> ) Product of Western Gold and Platinum Co., Belmont, California. (c) Al <sub>2</sub> O <sub>3</sub> was AD99 (99% Al <sub>2</sub> O <sub>3</sub> ) Product of Coors Porcelain Co., Golden, Colorado.									

## b. MATERIALS

Analyses of the various lots of beryllia ceramics, metals, and brazing alloys used on this program are listed in Appendix B.

Ceramics were inspected and dye checked for porosity and cracks (Appendix A, MP-1). Acceptable ceramics were then cleaned, clean fired, and stored in sealed polyethylene bags until used.

The columbium-1% zirconium metal members were cleaned (Appendix A, MP-2) just before assembly. Brazing alloys were obtained in several forms but most of the work was done with the powder form. Alloys for brazing were melted and comminuted or rolled by a contract source<sup>17</sup>. The alloys to be reduced to powder were turned on a lathe into small chips and the chips then reduced to powder in a diamond mortar. Throughout the turning and pulverizing operation precautions were taken to insure the purity of the powder.

Brazing alloy foils were prepared at the contract source<sup>17</sup> by conventional pack rolling techniques at elevated temperatures and final room temperature rolling to size. Two of these materials were on hand in the form of melted buttons (the method of melting is described later); the third alloy was prepared in the form of a 50-gram button from virgin material. The buttons were machined, placed in picture frame-type mild steel packs, painted with chrome oxide to prevent reactions between pack and core, and sealed by electron-beam welding to insure removal of the bulk of the nitrogen and oxygen. During the initial rolling sequence, which was accomplished at 1472° F (800° C), it was noted that when the pack containing the 40Zr-30Ti-30V alloy was reduced 66 percent (and the core reduced 58 percent) the pack ruptured. The initial rolling of the pack, containing the 50Ti-30Zr-20V alloy, ruptured after it was reduced 87 percent (and the brazing alloy core was reduced 83 percent). An examination of the cores at this stage of fabrication revealed some edge cracks and the remains of a solidification pipe in the 40Zr-30Ti-30V alloy. The 50Ti-30Zr-20V core appeared to be in excellent condition.

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<sup>17</sup>Battelle Memorial Institute, Columbus, Ohio.

After trimming the edges of the cores to remove all evidence of cracking and to obtain regular shapes, the cores were placed into new packs as before but with cover plates 0.130-inch thick. The 40 weight percent zirconium alloy pack was then reduced to 0.55-inch with an average core thickness of 0.030-inch. The 50 weight percent titanium alloy pack was rolled to 0.035-inch with an average core thickness of 0.007-inch. These brazing alloy cores were vapor blasted, belt sanded, and then cold-rolled on a four-high mill to 0.002-inch foil. Rolling was terminated at this point as no further reduction in thickness was noted after repeated passes through the rolls. Further reduction of the material might be possible by vacuum annealing and pack rolling. (It should be noted that there is no assurance that this would not yield wrinkled and torn material of little value.)

The alloy containing 56 weight percent zirconium, 28 weight percent vanadium, and 16 weight percent titanium was prepared in much the same manner as the aforementioned materials. A 50-gram button of the alloy was prepared from virgin melting stock. Melting was accomplished by the inert-gas nonconsumable arc-melting technique at 400 amperes for 30 seconds per melt utilizing a water cooled tungsten-tipped electrode. After melting six times, the button weighed 49.90 grams. This represents a loss of 0.2 percent during melting. The tungsten tip exhibited a weight gain of 0.02 grams as a result of these meltings. Experience indicates that there was little or no contamination due to tungsten in the button and an alloy of the same composition as the charge to the furnace resulted under these conditions. After melting the button was cleaned on a shaper, put in a pack, and rolled. Pack rolling was accomplished at 1650° F with reductions of 10 percent per pass. When the brazing alloy core was removed from the pack it was approximately 0.015-inch thick. The core was vapor blasted, belt sanded, and cold rolled to 0.002-inch-thick foil.

#### c. TEST SPECIMEN FABRICATION

##### (1) Components

Ceramic parts were obtained in a form ready to use after cleaning. The only additional preparation involved those specimens that were metallized before brazing. The evaporated molybdenum method was the one used in the selected systems. A detailed metallizing procedure and the apparatus are described in Appendix A, MP-1.

Metal parts for modulus-of-rupture, tab peel, and vacuum leak tightness specimens were punched from annealed Cb-1Zr sheet stock; then cleaned before fabrication.

## (2) Specimen Assembly

Specimens were assembled into graphite jigs in laminar air-flow hoods. The brazing alloy powder was prepared for use by mixing a small quantity with enough methacrylate to completely wet the powder, leaving some excess. Chemically pure acetone was used to thin the paste. The brazing paste was placed on the ceramic area to be brazed with a small spatula and allowed to dry. The amount applied was controlled strictly by the experience and judgement of the individual applying it. This was one of the most unsatisfactory steps in the process and was one of the two principal reasons for attempting to obtain brazing in foil or wire form. When brazing with foil, the proper size foil shape was punched from the foil, cleaned, and placed at the joint. A drop of methacrylate was used to position the foil on the ceramic.

## (3) Brazing

Because of the use of refractory metal parts and brazing alloys, only vacuum brazing was utilized. The system and procedure were previously (ref. II-1) described but are outlined below.

The furnace consisted of an induction-heated can assembly mounted in a vacuum bell jar (figure II-17). The cylindrical molybdenum cans were approximately five inches in diameter and five inches long. Inner molybdenum heat shields at top and bottom contained several large openings for vacuum pumping. The furnace temperature was monitored with Pt - Pt-10%Rh thermocouples located in the center of the can assembly and led in through the bottom center of the can with shielded leads. The can assembly was heated by radio frequency induction through the Vycor bell jar. The power supply was manually controlled through a magnetic amplifier from 0 to 25 kW at 30 MHz. The vacuum system was capable of maintaining  $2 \times 10^{-5}$  torr with a reasonably fast brazing cycle of one hour (plus cooling time).

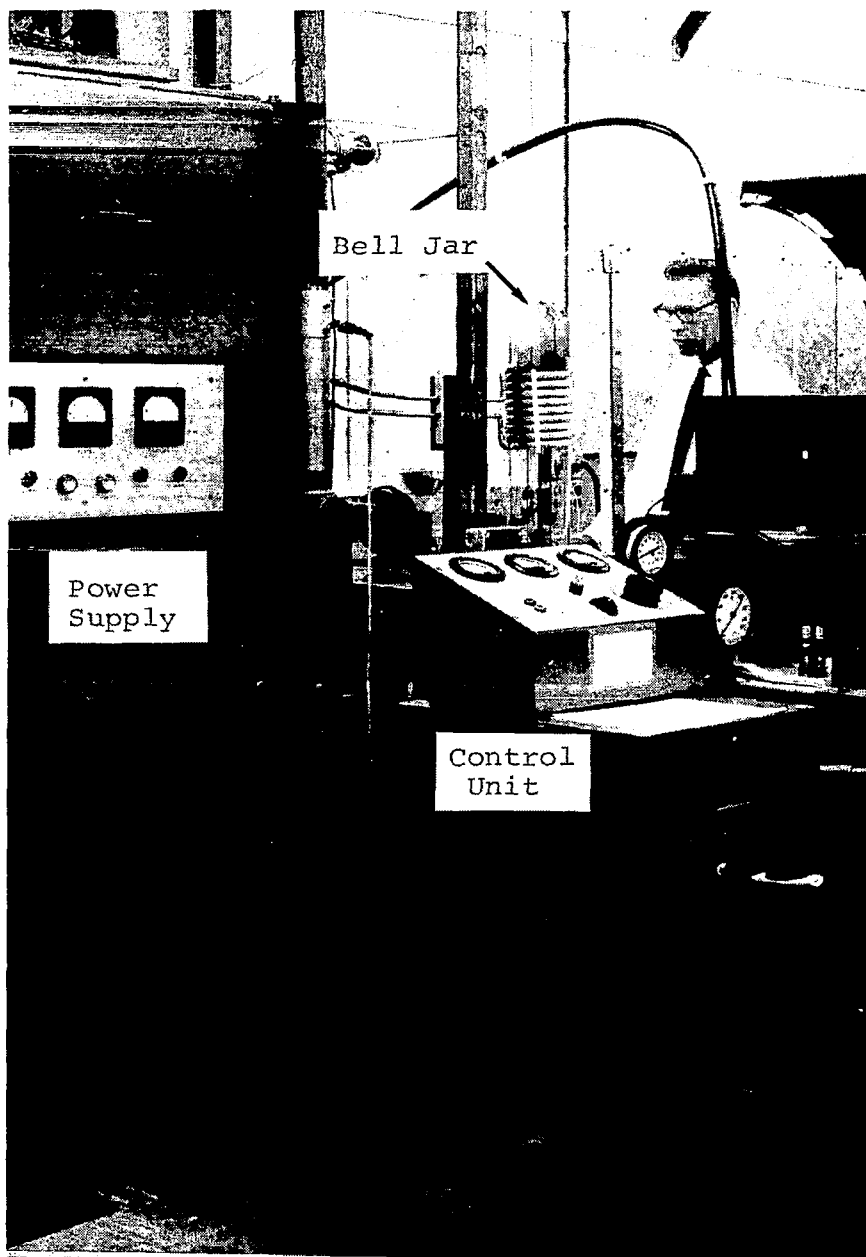


FIGURE II-17. Vacuum Brazing Furnace



After a modification part way through the project, the pressure could be maintained below the  $5 \times 10^{-6}$  torr level except for two periods. One was when baking out the methacrylate binder at  $575^{\circ}$  F. The other was when approaching the brazing temperature. Pressures could approach the  $1 \times 10^{-5}$  torr level depending on the furnace load during these two periods. The specimens were generally cooled to room temperature in vacuum, although inert gas was introduced occasionally to accelerate cooling below  $400^{\circ}$  F.

Decomposition and removal of the methacrylate binder was one of the major time consuming factors in the brazing schedule. From 1/2 hour to 2 hours were usually required in the  $200^{\circ}$  to  $650^{\circ}$  F range. If the temperature increased rapidly powder was ejected from the brazing region. After the methacrylate binder was eliminated, the temperature could be raised quite rapidly without driving the pressure above  $2 \times 10^{-5}$  torr, or  $5 \times 10^{-6}$  torr after the furnace was modified. The brazing cycle included two hold periods. One hold period was for 10 minutes at a temperature of about  $180^{\circ}$  F below the melting point of the alloy to permit all parts to heat uniformly and outgas; the temperature was then raised rapidly to the brazing temperature and held for five minutes before turning the power off.

### 3. The Microstructure of Selected Ceramic-to-Metal Seals

#### a. THE MICROSTRUCTURE OF THREE CERAMIC-TO-METAL SEAL SYSTEMS

An analysis of the microstructure was made on samples of vacuum tight BeO to Cb-1Zr assemblies fabricated with three braze alloys (56Zr-28V-16Ti, 75Zr-19Cb-6Be, and 48Zr-48Ti-4Be). These systems had shown promise after 500-hour,  $1600^{\circ}$  F exposure tests in potassium (ref. II-1).

Sections from these seals were subjected to microhardness tests, electron-microprobe analysis, and micrographic studies.

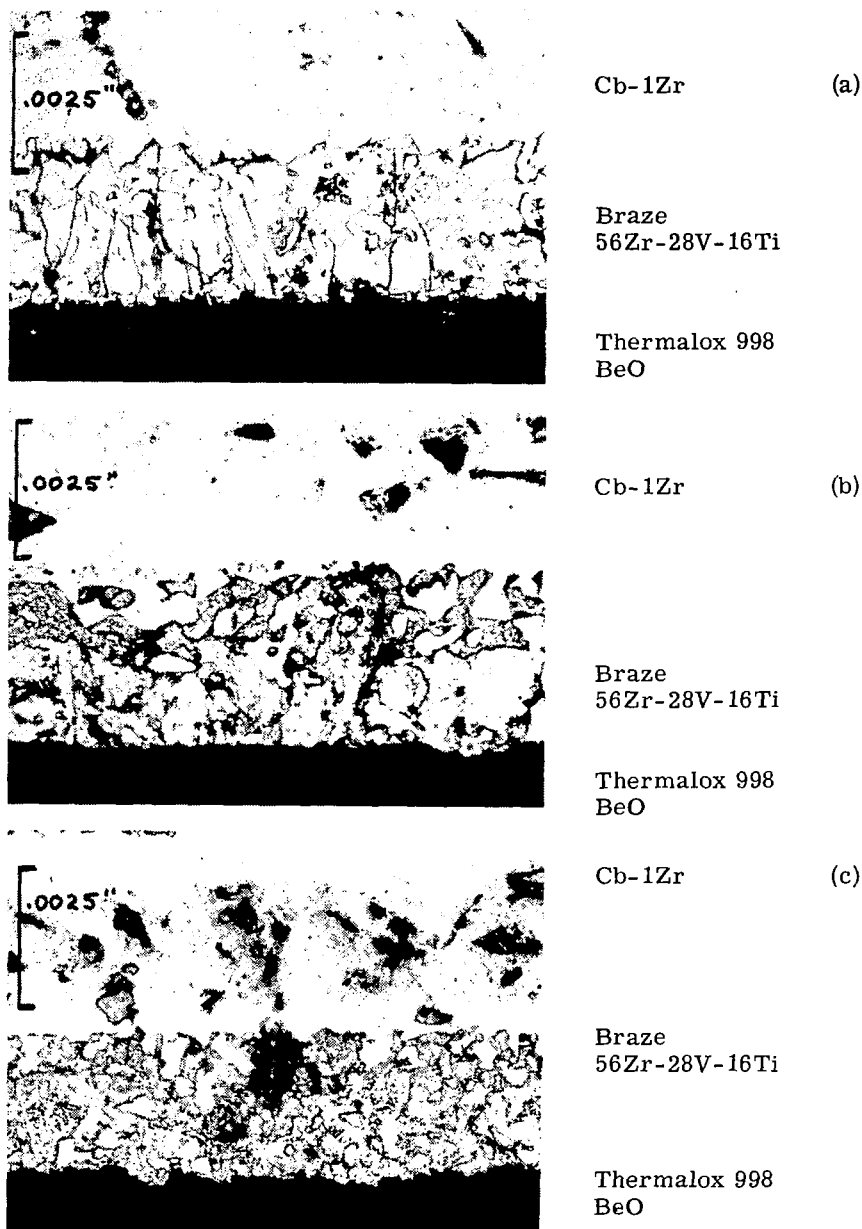
##### (1) The BeO (56Zr-28V-16Ti) Cb-1Zr System

Sections of BeO to Cb-1Zr seals brazed (brazing temperature  $2372^{\circ}$  F) with active alloy 56Zr-28V-16Ti were examined in the as-brazed condition and after 500 hours exposure at  $1600^{\circ}$  F to potassium vapor

and vacuum. A microprobe trace was made on the potassium exposed sample only. Microstructures from the three conditions are shown in figure II-18. Differences in microstructure exist in each case. Three or four phases, in some cases, are visible in the brazement. Microhardness (table II-5) and electron microprobe data (figure II-19) indicate two separate phases. The first (brown) phase is rich in Zr and is quite hard. The second (white) phase is soft but has substantially different compositions in the two locations, being richer in Cb next to the Cb-1Zr metal member. However, it may be noted from the composition listed in figure II-19 that the V-Ti ratio is identical in the two locations. A scan for potassium and titanium showed no potassium within the discrimination limits of the microprobe equipment (<230 ppm); and 8 percent, 18 to 23 percent, and 29 percent titanium in phases 1, 2b, and 2a respectively.

TABLE II-5. Microhardness Test Results on 56Zr-28V-16Ti Alloy  
Braze to Cb-1Zr and 99.8 Percent Beryllia

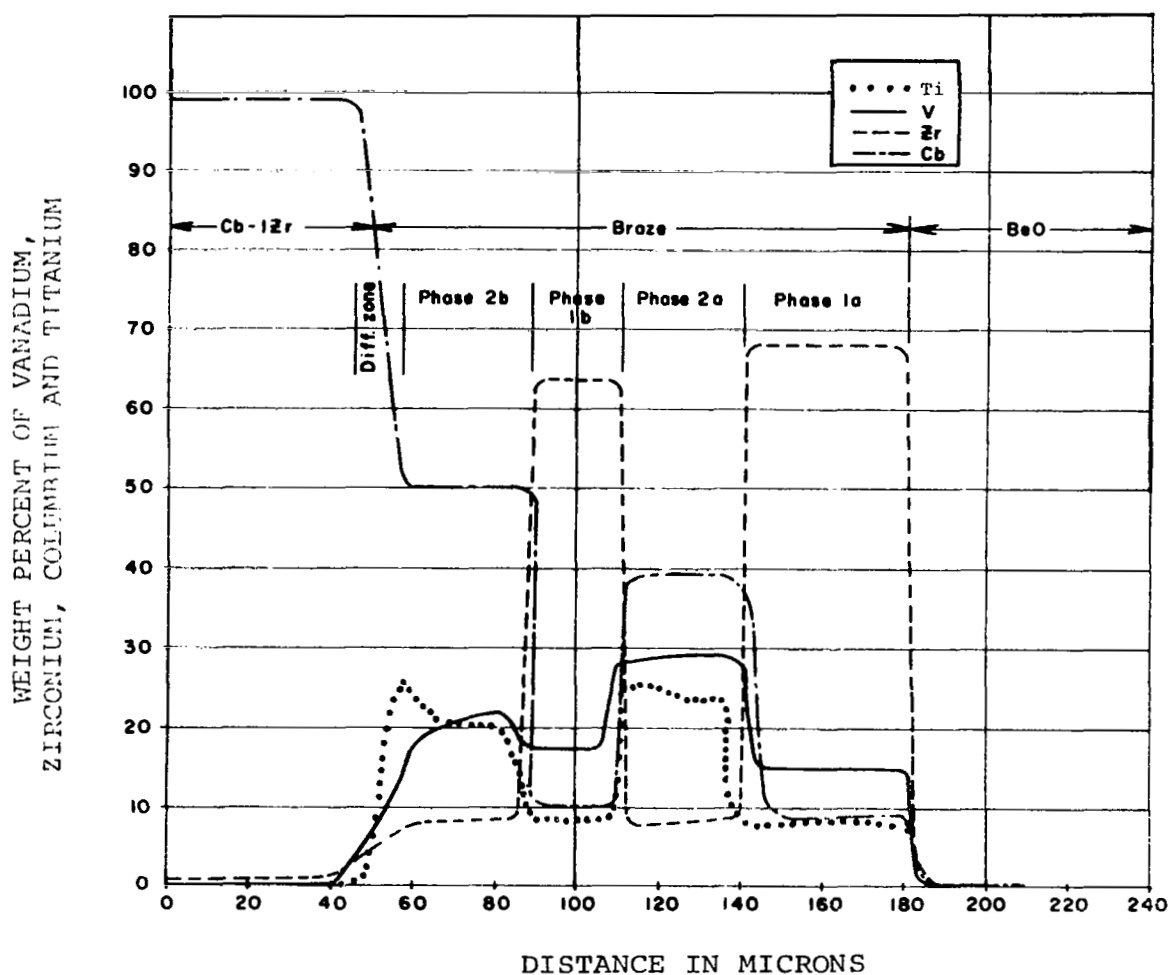
Phase Designation(a)	Knoop Hardness (50g load)		
	Sample 1 As brazed	Sample 2 Vacuum Exposed(b)	Sample 3 Potassium Exposed(b)
Cb-1Zr	113	139	160
Interface 2b	357	364	450
Brown phase 1a + 1b	-	1235	780-900
White phase 2a	407	211	(c)
Interface phase	1140-1300	-	-
Ceramic (BeO)	1140	-	-
(a) For phase area and compositions, see figure II-19 (b) 1600° F, 500 hours (c) Too small in unit size to determine			



Etchant: 30 ml lactic acid, 10 ml  $\text{HNO}_3$ , 10 ml HF

Note: Samples shown are the samples used for the microhardness and microprobe analyses described in the accompanying text. (a) as brazed, (b) vacuum exposed for 500 hours at 1600°F, (c) potassium exposed 500 hours at 1600°F, different specimen used for microprobe analysis shown in Figure IV-6.

**FIGURE II-18. Photomicrographs of Alloy 56Zr-28V-16Ti Brazements Between Cb-1Zr and Thermalox 998 (99.8% BeO) (400X Before Photo Reduction)**



Sample was Potassium Exposed for 500 hours  
at 1600°F, no potassium detected by micro-  
probe, limit of detectability - 230 ppm.

FIGURE II-19. Plot of Electron Microprobe Scan Across  
Alloy 56Zr-28V-16Ti Braze Between Cb-12r  
and Thermalox 998 (99.8% BeO)

It was first believed that the soft white phase was Cb-Ti-V-Zr solid solution which had partially transformed to an eutectoid on cooling. The harder phase was believed to be the  $ZrV_2$  solid solution eutectic. This interpretation was consistent with the fact that each apparent phase was previously noted to be made up of two phases.

The final interpretation is substantially different from the first evaluation and begins with consideration of the binary systems (table II-2). Only one intermetallic compound ( $ZrV_2$ , forming from a monotectic at 2372° F) is certain in the Zr, Cb, Ti, V system. The compositions, determined by electron microprobe analysis as weight percent, when converted to atomic percent, (figure II-19) show that only approximately 1/5 of the Zr in phase 1 can be tied up as  $ZrV_2$ ; even less if a ternary compound exists. The majority of the Zr must therefore be accounted for in some other form.

The brazing alloy was originally formed during arc-melting as a eutectic between  $ZrV_2$  and  $\beta$  (Zr, Ti), the phase being Zr-rich. Much of the V may also have remained in the  $\beta$  phase. Solid phase transformations from  $\beta$  to  $\alpha$  also probably occurred. The presence of Ti probably increases the solubility of V in  $\beta$ -Zr, thus moving the V-Zr solidus toward higher V content. When the alloy was remelted during brazing, the eutectic was then located on the V-rich side of the alloy composition so that the melt consisted of a large amount of unmelted  $\beta$ -Zr, and liquid rich in V and Ti (all the  $ZrV_2$  would have melted.) When the Cb constituent started to dissolve into the melt, the solidus of the quaternary system was reached locally, causing precipitation of the  $\beta$  (Cb, Ti, V) with the small amount of Zr in the melt also in solid solution. This was the soft phase 2 indicated in figure II-19. The constant Cb content shown by the microprobe scan of phase 2 indicates that it must have formed from the melt, otherwise a gradient would be shown. Some solid phase diffusion must have occurred also as indicated by the steep gradients at the edge of the phases. When the temperature was reduced, the remainder of the melt solidified leaving a matrix of the originally unmelted  $\beta$  (Zr, Ti) plus a new  $\beta$ -Zr solid solution containing Cb, V, and Ti, plus the  $ZrV_2$  compound.

The hardness may be due to a fine precipitate. This could have occurred during the 1600° F exposure.

## (2) The BeO (75Zr-19Cb-6Be) Cb-1Zr System

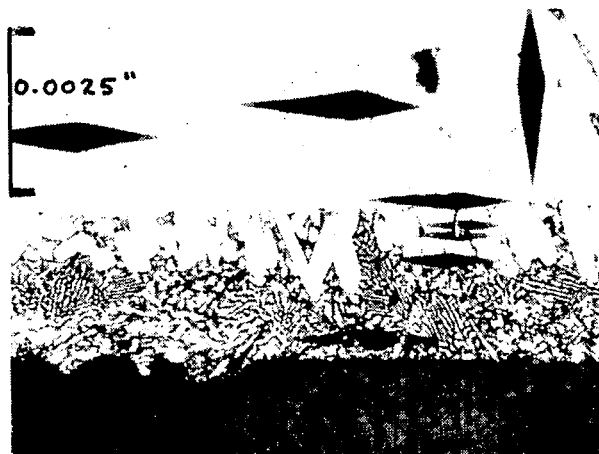
Sections of BeO to Cb-1Zr seals brazed (brazing temperature 1985° F) with active brazing alloy 75Zr-19Cb-6Be were examined in the as-brazed condition and after 500-hour exposure at 1600° F to potassium vapor and vacuum.

Microstructures of samples from the three exposure conditions are shown in figure II-20. Two phases are visible, a crystalline phase growing from the Cb-1Zr surface and an eutectic matrix. Microhardness data presented in table II-6 and analysis obtained by microprobe (figure II-21) confirm the two phases. The Cb-rich phase next to the metal member was harder than a similar phase 1 in the 56Zr-28V-16Ti system.

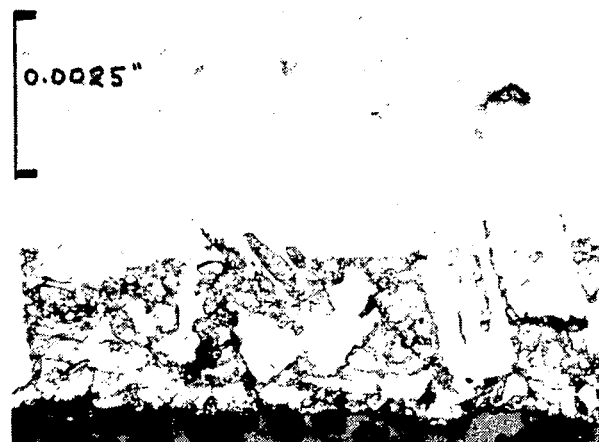
It is postulated that the white phase forms in the same manner as indicated for the white phase in the seal system reported in the preceding paragraphs; by solidifying from the melt as the columbium dissolves and the solidus is reached locally. However, the great discrepancy in hardness between the two systems is unresolved.

The microprobe analysis may be in error. Since the Be content by microprobe was determined by difference there may be an error of six percent. It may be noted that the average composition of the phase 2 constituent compared to the starting composition of the brazing alloy leaves a net loss of Zr and a gain in Be, an unlikely occurrence. In fact some loss of Be by vaporization during brazing is likely.

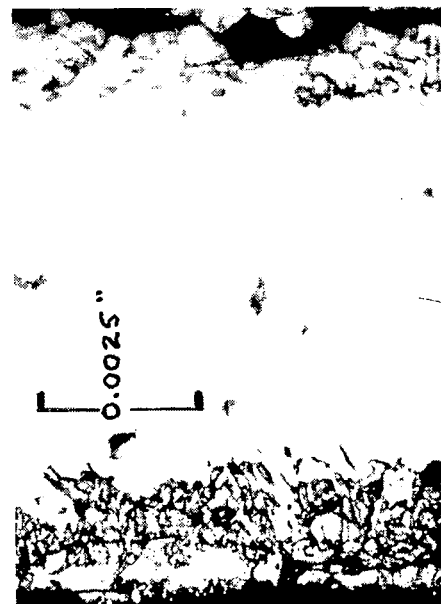
It was significant that in the as-brazed sample, the eutectic phase indicated low microhardness values in as close proximity to the BeO as can be measured. There was no noticeable visual or hardness change even with the significant decrease in Zr content that began 10 microns from the phase boundary, a distance that is discernible in the micrographs.



(a)  
Cb-1Zr  
  
Braze  
75Zr-19Cb-6Be



Thermalox 998  
BeO  
  
Cb-1Zr  
  
(c)  
Cb-1Zr  
  
Braze  
75Zr-19Cb-6Be  
  
Thermalox 998  
BeO

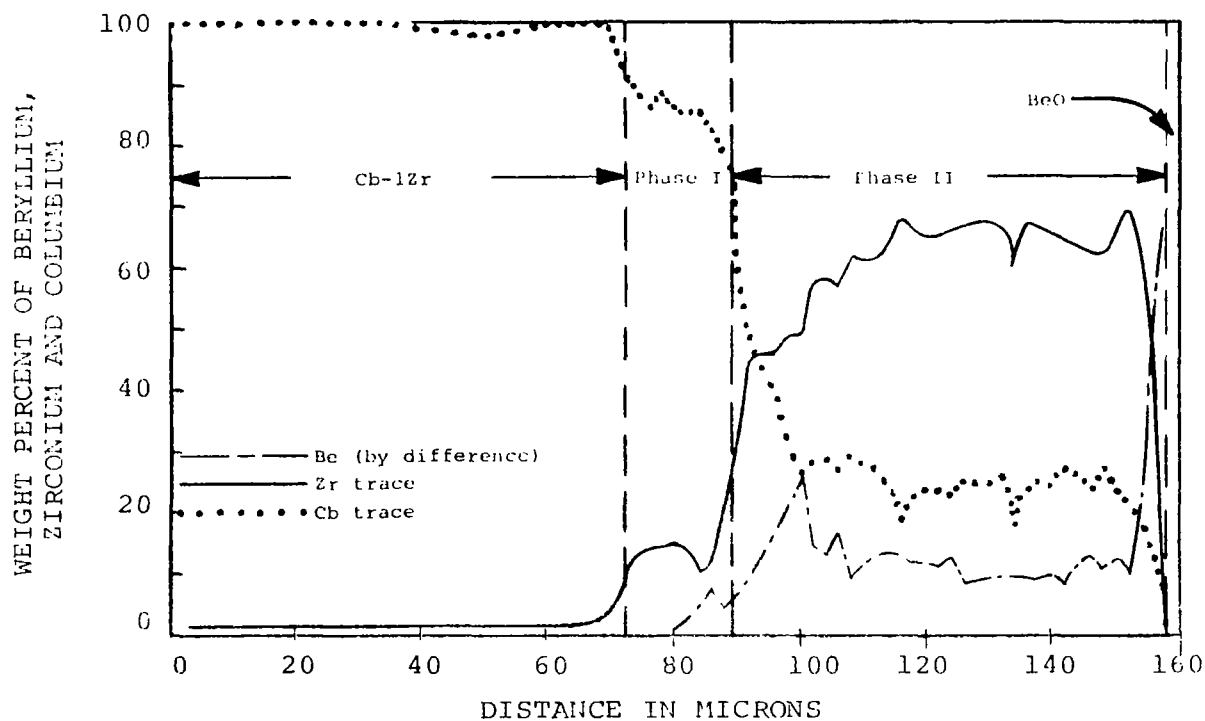


(b)  
Thermalox 998  
BeO  
  
Braze  
75Zr-19Cb-6Be  
  
Cb-1Zr  
  
Braze  
75Zr-19Cb-6Be  
  
Void

Etchant: 30 ml lactic acid, 10 ml  $\text{HNO}_3$ , 10 ml HF

Note: Samples shown are the samples used for the microhardness and microprobe analyses described in the accompanying text. (a) as brazed, (b) vacuum exposed 500 hours at 1600°F, (c) potassium exposed 500 hours at 1600°F.

FIGURE II-20. Photomicrographs of Alloy 75Zr-19Cb-6Be Brazements Between Cb-1Zr and Thermalox 998 (99.8% BeO) (400X Before Photo Reduction)



Sample was in the as-brazed condition

FIGURE II-21. Plot of Electron Microprobe Scan Across Alloy 75Zr-19Cb-6Be Braze Between Cb-1Zr and Thermalox 998 (99.8% BeO)



TABLE II-6. Microhardness Test Results on Five Assemblies of 99.8 Percent Beryllia Joined to Cb-1Zr Alloy with Braze 75Zr-19Cb-6Be

Phase Designation	Knoop Hardness (50g load)				
	Sample 1 As brazed	Sample 2 Vacuum Exposed(a)	Sample 3 Potassium Exposed(a)	Sample 4 As brazed	Sample 5 Potassium Exposed(b)
Cb-1Zr	150	120	151(d), 137	150	157
Interface	350	300	260(d), 319	211	384
Crystal phase	1040	750	813(d), 785	1052	914
Eutectic	284-312	(c)	(c)	497	400, 600
Interface	284-312	820	974(d), 846	463	1138
Ceramic (BeO)	1140				
(a) 1600°F for 500 hours (b) 1000°F for 500 hours (Ei-3-3) (c) Not Determined, too small an area (d) 15g load, otherwise 50g load used					

TABLE II-7. Microhardness Test Results on 99.8 Percent Beryllia to Cb-1Zr Alloy Assemblies Brazed with 48Ti-48Zr-4Be

Phase Designation	Knoop Hardness (50g load)		
	Sample 1 As brazed	Sample 2 Vacuum Exposed(a)	Sample 3 Potassium Exposed(a)
Cb-1Zr	120	152	148
Interface	314	465	463
Crystal	411	433	425
Eutectic or	512	>445(b)	-
black crystal phase	-	-	1344
Interface crystal	726	456	425
Ceramic (BeO)	1140		
(a) 1600°F, 500 hours (b) very small area			

### (3) The BeO (48Zr-48Ti-4Be) Cb-1Zr System

Microstructures of samples from the BeO (48Zr-48Ti-4Be) Cb-1Zr system (brazed at 2030° F) in three exposure conditions are shown in figure II-22. As confirmed by microhardness data (table II-7) and microprobe analysis (figure II-23), a crystalline phase occurs next to the ceramic and metal members with an eutectic matrix between.

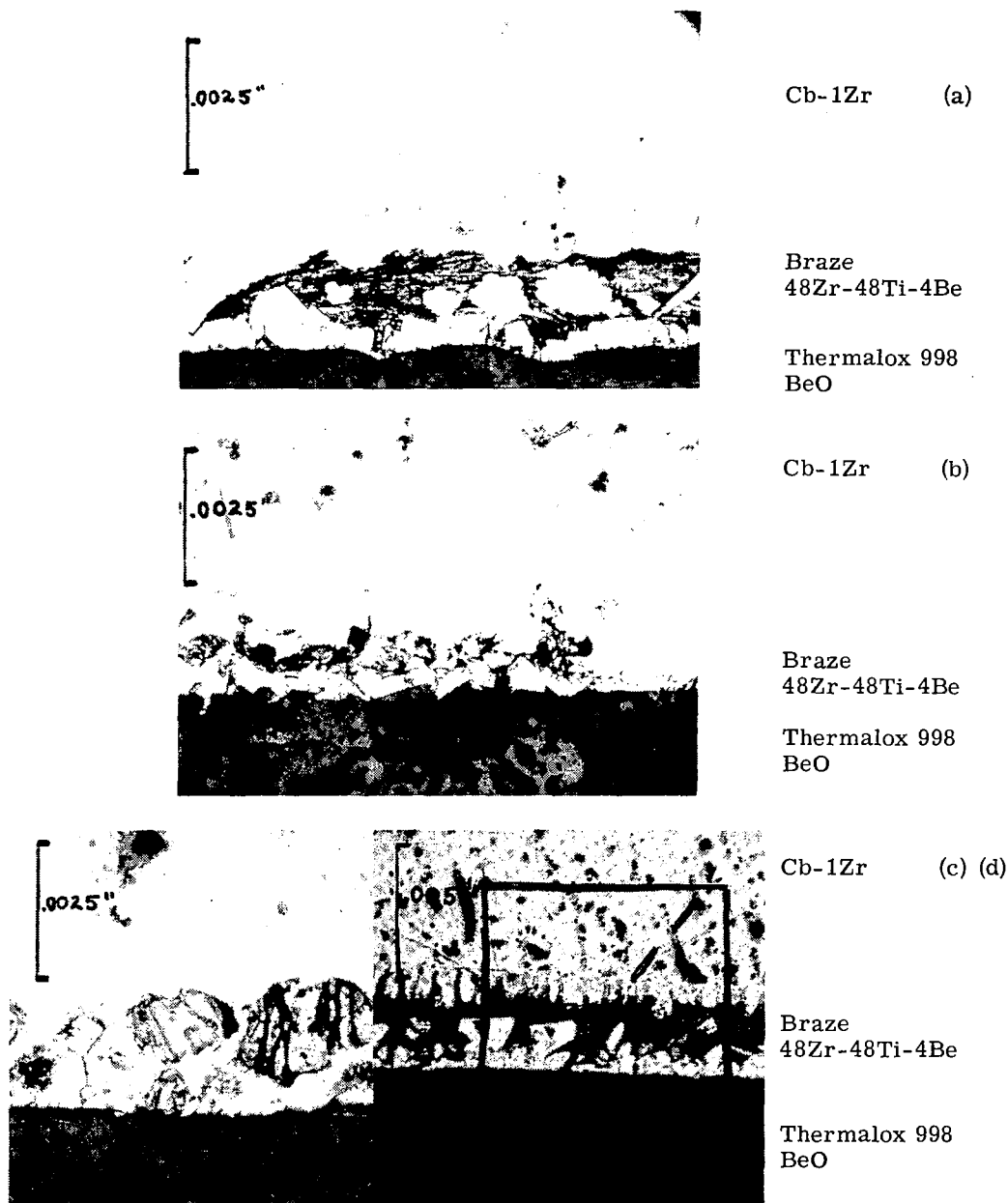
In general, the phases in this system are softer than those in the Zr-Cb-Be alloy system with the exception of small areas of a hard, black intermetallic found in the potassium-exposed sample. The intermetallic was formed at the expense of the eutectic phase noted in the other samples. The white crystal phase in the as-brazed sample (figure II-22a) may be intermetallic but is soft enough in the vacuum and potassium-exposed samples (figure II-22b and II-22c) to indicate a Cb-Zr-Ti solid solution phase was forming as a result of extensive Cb diffusion into the brazement.

The crystalline phase III, next to the beryllia ceramic, is the hardest of the phases at 726 knoop hardness. Its composition by microprobe analysis is 10% Cb, 10 to 35% Zr, 45% Ti and 0 to 35% Be; the latter increasing toward the BeO interface with a corresponding decrease in Zr.

#### b. DIFFUSION OF BRAZING ALLOY CONSTITUENTS INTO THE METAL MEMBER

Diffusion of the brazing alloy elements into the metal member was observed for all three systems. The approximate diffusion distances determined from the electron microprobe scans are given below.

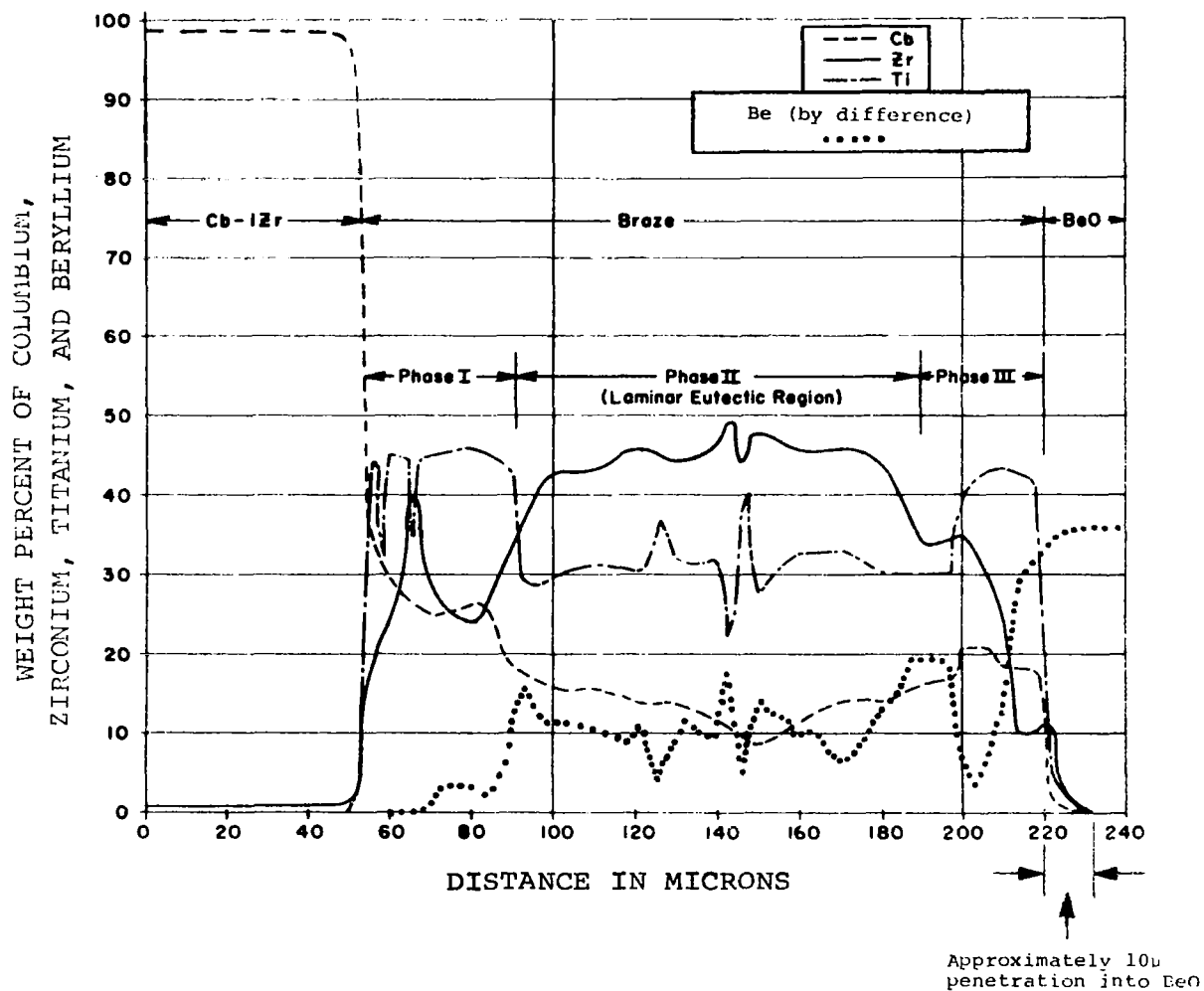
<u>Alloy</u>	<u>Diffusion Distances</u>	<u>Brazing Temperature</u>	<u>Time at Brazing Temperature</u>	<u>Condition</u>
75Zr-19Cb-6Be	4μ	1985° F	5 min.	As-brazed
48Zr-48Ti-4Be	4μ	2030° F	5 min.	After 500-hour, 1600° F potassium exposure
56Zr-28V-16Ti	15μ	2372° F	5 min.	After 500-hour, 1600° F potassium exposure



Etchant: 30 ml lactic acid, 10 ml  $\text{HNO}_3$ , 10 ml HF

Note: Samples shown are the samples used for microhardness and microprobe analyses described in the accompanying text. (a) as brazed, (b) vacuum exposed 500 hours at  $1600^\circ\text{F}$ , (c) potassium exposed 500 hours at  $1600^\circ\text{F}$ , (d) as for (c), dotted line shows path of microprobe trace.

FIGURE II-22. Photomicrographs of Alloy 48Zr-48Ti-4Be Brazements Between Cb-1Zr and Thermalox 998 (99.8% BeO) (abc400X, d200X Before Photo Reduction)



Sample was K exposed for 500 hours at 1600°F

FIGURE II-23. Plot of Electron Microprobe Scan Across Alloy 48Zr-48Ti-4Be Braze Between Cb-1Zr and Thermax 998 (BeO)

These distances are somewhat arbitrary as in each case a solid solution crystal phase grew from the interface. However, the microhardness traverses (tables II-5, II-6, and II-7) indicate that some elements diffuse for greater distances into the specimen than given above (not detected by the microprobe). If this is not the case, then the increased hardness toward the Cb-1Zr at the braze interface may be due to interstitial elements picked up by diffusion from the brazing alloy.

It is highly improbable that beryllium diffused appreciably into the columbium lattice. Studies of the binary Cb-Be system (refs. II-8 and II-9) show that a diffusion couple of Cb and Be metal members will form a layered structure with the properties as shown in table II-2.

#### 4. Development of Alternate Braze Sealing Systems

##### a. DEVELOPMENT OF NEW BRAZING ALLOYS

Three yttrium alloys, Y-6Cb, Y-6Be and Y-46Zr were selected for brazing tests because of the thermodynamic stability of  $Y_2O_3$  in the presence of alkali metals and because of the scavenging effect of yttrium in columbium alloys.

Yttrium brazing alloy studies were started by brazing three-mil yttrium metal foils<sup>18</sup> to Cb-1Zr and beryllia or alumina CLM-15 tensile test pieces. Good mechanical seals were obtained with brazing cycles at 2550° F under a vacuum of  $1 \times 10^{-4}$  torr at that temperature. However, leak checks showed the alumina sample to have a micro-leak while the beryllia sample indicated a gross leak.

Yttrium metal foil was placed on an alumina substrate and processed under the same conditions as above (in vacuum at 2550° F). Despite the fact that yttrium melts at 2680° F, a firm mechanical bond was established between the yttrium and the alumina member; thus indicating that considerable reduction of alumina had taken place.

Two samples of yttrium-6% Cb brazing alloy (using Y and Cb-1Zr shims) on BeO and  $Al_2O_3$  plaques were processed at 2550° F in vacuum as above. Although neither alloy melted, it was noted that the reaction had proceeded much further on the alumina plaque than on the beryllia plaque; thus indicating that reduction of alumina to aluminum occurred more readily than beryllia to beryllium, and the consolidation of the brazing alloy must have been due to solution of aluminum in the brazing alloy. These results might be

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<sup>18</sup> Obtained from Battelle Memorial Institute, Columbus, Ohio.

expected, considering the relative thermodynamic stability of  $\text{Al}_2\text{O}_3$  and  $\text{BeO}$ . The above braze was tested on a Cb-1Zr plaque. Only partial melting took place under the same conditions where no melting took place on the ceramic plaques. In order to investigate the effect of the zirconium from the Cb-1Zr alloy on this braze alloy, an eutectic melt of Y-46Zr with a melting point of  $2525^\circ \text{F}$  was used to join a Cb-1Zr washer to  $\text{Al}_2\text{O}_3$ . A good mechanical seal was obtained. However, difficulty was experienced in evacuating the seal which indicated a poor hermetic seal. The alloy foils had melted down adequately, but the braze appeared to be granular and porous.

Work was not continued on yttrium or yttrium alloy brazes because of the high brazing temperatures required in relation to the sintering and deformation temperatures of thin-wall beryllia shapes. In addition, interstitial analysis results showed high oxygen content in the yttrium and Cb-1Zr foils.

Yttrium is still of interest, despite its relatively high vapor pressure, and relative impurity level in this test because of the high stability of  $\text{Y}_2\text{O}_3$  and of the intermetallic compounds of yttrium. It may be of particular value as a ceramic wetting layer (to concentrate its effect at the brazement/ceramic interface) or as a minor constituent of a brazing alloy.

b. PROCESS MODIFICATION AND TESTING OF SELECTED BRAZING ALLOYS

(1) Alternate Forms of Brazing Alloys

The oxide content of the ceramic-brazement interface (resulting from oxides in the brazing alloy, from occluded atmospheric gases in the brazing alloy, and from reaction of the brazing alloy with the ceramic substrate) represents a potentially vulnerable area in the overall ceramic-metal sealing system. The oxides of columbium, zirconium, titanium and vanadium in the braze material are much less stable in alkali-metal vapor than the metals themselves, while nitrogen or nitrides accelerate corrosion by lithium. The contributions of the three oxygen (and nitrogen) sources mentioned above can be controlled in a seal by the methods described below:

- a) Oxides (or nitrides) in the brazing alloy can be controlled by using pre-analyzed low-oxygen materials and high quality

TABLE II-8. Summary of Brazing Data for the Selection of Braze Alloys to Join Thermalox 998 Beryllia Ceramic to Columbium-13 Zirconium Metal

Nominal Alloy Composition (weight percent)	Brazing Conditions Time (minutes)    Temperature (°F)		Strength of Braze Specimens								Leak Test(e)
			Room Temperature Modulus of Rupture				Room Temperature Tab Peel Strength				
			Number of Specimens	Remarks	Average Strength (psi)	Standard Deviation(d) (psi)	Number of Specimens	Remarks	Average Strength (pounds. inch)	Standard Deviation(d) (pounds. inch)	
68Ti-28V-4Be	5	2372	14	(a)	17,465	1,900	6	(c)	9	2	6/8 VT
46Ti-46Zr-4Be-4V	5	1832	17	(a)	16,800	3,220	8	(a)	19	17	5/6 VT
50Zr-30V-20Cb	5	2516	6	(a)	15,150	2,160	4	(b)	21	3	2/2 VT
60Zr-25V-15Cb	5	2436	12	(a)	15,000	875	6	(b)	34	9	6/6 VT
50Zr-30Ti-20V	10	2732	4	(b)	15,225	3,140	2	(b)	21	±1 (f)	0/2 VT
35Ti-35V-30Zr	1	2804	3	(a)	24,437	1,380	2	(c)	16	±0 (f)	2/8 VT

Ceramic parts were Brush Beryllia's 99.8% BeO body containing 70 ppm SiO<sub>2</sub> (Lot No. F) or 150 ppm SiO<sub>2</sub> (Lot No. E). The parts were fabricated by dry pressing slabs, firing in electric kiln with subsequent cutting and grinding to shape. The ceramic bar size was 0.1 inch x 0.1 inch x 1 inch. Density was between 2.85 and 2.94 g/cc as specified by vendor. Average post-braze modulus-of-rupture strength of the ceramic was 25,000 psi. Ten bars from above assemblies were tested. The standard deviation was 3230 psi. The metal member was 0.015 inch thick Cb-1%Zr sheet.

Note:

- (a) Good wetting, good fillet.
- (b) Fair wetting, incomplete fillet.
- (c) Poor wetting, incomplete, granular fillet.

$$(d) S = \sqrt{\frac{\sum (x - \bar{x})^2}{(n-1)}}$$

(e) VT indicates a leak rate < 1 x 10<sup>-9</sup> std. cc/sec., 2/3 indicates 2 of 3 samples vacuum tight, etc.

(f) When there were less than three specimens, the standard deviation was not determined; the value shown indicates the spread of values from the average value.

The strength data in table II-8 do not include test results on every brazed specimen because it was occasionally found that some joints in the same brazing run were abnormally low in comparison with the general strength level. It was possible to detect and reject the low-strength brazed samples on the basis of visual appearance prior to testing. The causes for rejection were primarily due to faulty assembly which included misalignment, faulty pressure application, or loss of brazing alloy powder. A smooth well-filleted braze was not obtained in every instance, however, because certain alloys were characterized by incomplete or uneven wetting. It is probable that in these cases, the poor wetting could be alleviated by using a metallic wetting layer on the beryllia ceramic. Some process variations were carried out whenever the brazements appeared to be less than optimum.

In addition to the braze filler alloy evaluations, several beryllia ceramics were tested to obtain the modulus-of-rupture strength of these bodies. The tested ceramic pieces were the end portions of modulus-of-rupture assemblies and had been exposed to the indicated brazing cycle as well as the normal ceramic cleaning and firing steps. This procedure was followed in order to include the possible influence of brazing temperature exposure on ceramic strength. The strength of the brazed modulus-of-rupture assembly could also be compared directly to that of the ceramic.

(a) Brazing Alloy 68Ti-28V-4Be

Brazing alloy 68Ti-28V-4Be was the only braze alloy of the six tested that contained no zirconium. The average modulus-of-rupture strength was 17,465 psi. On the deficit side, the braze alloy showed poor wetting, forming isolated droplets, and had an average tab peel strength of only nine pounds per inch. Of the six alloys tested, this alloy showed a leakage incidence second only to that of the 50Zr-30Ti-30V alloy. The poor wetting was due in part to an increase in surface tension and melting point due to the loss of beryllium by volatilization. The vapor pressure is reported (ref. II-12) to be near  $10^{-2}$  torr at 2239° F (1226° C) which is less than the brazing temperature 2372° F (1300° C). Volatilization is not necessarily detrimental since it is a



conventional method of raising the melting point of a braze by removing a melting point depressant, in this case, beryllium. The volatilization could be inhibited by brazing in an inert atmosphere, although contamination by reactive gases would be greater than that encountered in vacuum brazing. It is also possible that wetting and liquid spreading could be improved in this case by metallizing the ceramic or altering the brazing cycle.

The low-average tab peel strength for the 68Ti-28V-4Be brazing alloy was apparently related to poor wetting of both the metal and ceramic. It was noted that an increase in applied pressure during brazing improved the peel strength slightly. It is possible that the low tab peel strength is indicative of the presence of a brittle layered phase, since a brittle layer would be conducive to crack propagation.

The mode of fracture of the tab peel specimens was not apparent from microscopic examination. The alloy was selected for potassium exposure testing because brazed specimens exhibited high strength. It was believed that the wetting characteristics could be improved by metallizing the ceramic with evaporated molybdenum.

#### (b) Brazing Alloy 46Ti-46Zr-4Be-4V

Brazing alloy 46Ti-46Zr-4Be-4V appeared particularly promising for bore seal applications in the 1000° to 1400° F temperature range because of its excellent wetting and relatively low brazing temperature (1832° F). Like the 68Ti-28V-4Be alloy, this alloy contained beryllium which would be expected to form a suitable joint with the beryllia. This alloy was selected for further evaluation by potassium exposure testing.

#### (c) Brazing Alloy 60Zr-25V-15Cb

Beryllia to Cb-1Zr specimens brazed with the 60Zr-25V-15Cb alloy showed an average tab peel strength of 34 pounds per inch, the highest average value of all six alloys tested. In general, the alloy appeared to form a very satisfactory brazement, with all leak test cylinders being vacuum tight. The alloy was

selected for potassium exposure testing.

This alloy, (60Zr-25V-15Cb), was selected for potassium exposure testing over the 50Zr-30V-20Cb primarily on the basis of its slightly lower brazing temperature, 2436° F (1330°C) versus 2516° F (1380°C). The lower brazing temperature of the 60Zr-25V-15Cb alloy was due to the lower columbium content.

(d) Brazing Alloy 50Zr-30V-20Cb

The 50Zr-30V-20Cb alloy was very similar to the 60Zr-25V-15Cb alloy in composition and test results. A comparison of compositions indicates that the 50Zr-30V-20Cb alloy is less reactive than the 60Zr-30V-15Cb alloy so wetting of the ceramic might be improved with an evaporated molybdenum wetting layer. The average tab peel strength of specimens made with the 50Zr-30V-20Cb alloy was slightly less than that of specimens made with the 60Zr-25V-15Cb alloy.

(e) Brazing Alloy 50Zr-30Ti-20V

Specimens brazed with the 50Zr-30Ti-20V alloy showed very satisfactory test results in preliminary tests but test results obtained later were not satisfactory. The earlier average modulus-of-rupture strength was near 25,000 psi (the basic strength of the ceramic) as opposed to the later value of 15,225 psi. The average tab peel results were similarly reduced from 49 pounds per inch to 21 pounds per inch. Neither of the two cylindrical assemblies which were made were vacuum tight. An apparent change in composition occurred when additional powder from the melt ingot was added to the first alloy powder. Since the composition of this alloy is similar to alloy 56Zr-28V-16Ti, which was scheduled for further test, the 50Zr-30Ti-20V alloy was not selected for additional tests.

(f) Brazing Alloy 35Ti-35V-30Zr

Specimens brazed with alloy 35Ti-35V-30Zr were the only specimens in this evaluation test to utilize a molybdenum wetting layer on the beryllia ceramic. This system exhibited the

highest average modulus-of-rupture strength (24,437 psi) of the six alloys tested. However, the alloy was rejected because of the high incidence of vacuum-leak failures. The fact that the brazing temperature of 2804° F was the highest of the alloys, was another consideration in its rejection. Mechanical deformation and sagging of large, thin-wall tubes would be expected at this temperature. However, this alloy, with additional testing, may be found suitable for relatively thick-wall structures.

### (3) Optimizing the Brazing Cycle of Selected Brazing Alloys

Ceramic-to-metal specimens brazed with active brazing alloys 56Zr-28V-16Ti and 48Zr-48Ti-4Be were subjected to brazing time and temperature variations. These alloys had previously (ref. II-1) shown alkali-metal compatibility after 500-hour exposure at 1600° F.

Microstructural variations could not be satisfactorily resolved solely on the basis of post-brazing exposure times and environments. The first objective of this work was to determine microstructural and flexural strength variations due to brazing temperature and brazing hold time differences which are greater than those encountered during normal active-metal brazing operations. The second objective was to determine whether the observed effects correlated with the wetting of the ceramic by the brazing alloy. Later, during the braze diffusion study, the newer 60Zr-25V-15Cb brazing alloy was included because of its desirable ductility. The brazing temperature for these alloys had been determined previously (ref. II-1) by trial braze runs at successively higher temperatures until satisfactory fillets, a high percentage of vacuum tight seals, and strength were obtained.

The standard vacuum brazing schedule used on this program consisted of a ten-minute hold at approximately 180° F below the brazing temperature of the alloy system, allowing the temperature to equalize within the furnace and allowing the vacuum to improve. The temperature was then rapidly raised to the predetermined brazing temperature, held for five minutes and the furnace power turned off. During the entire operation, the pressure in the furnace was held below  $5 \times 10^{-5}$  torr. After modification of the vacuum brazing furnace during this program, a pressure less than  $5 \times 10^{-6}$  torr was maintained.

For the diffusion brazing study on these first two alloys, the hold time at the brazing temperature was evaluated at zero minutes (actually one to five seconds), five minutes, and thirty minutes. The brazing temperature with the standard five-minute hold was evaluated at the predetermined temperature for each alloy and at 90° F (50° C) and 180° F (100° C) higher temperatures to accelerate diffusion. The test pieces consisted of ASTM CLM 15 geometry, Ei-3W alumina (99.7% Al<sub>2</sub>O<sub>3</sub>), pieces of Thermalox 998 beryllia (99.8% BeO) modulus-of-rupture bars and cylindrical vacuum-test specimens. The ceramic members were joined to a Cb-1Zr metal member with the respective brazing alloys. Tests were run in triplicate. The results of strength and vacuum integrity tests on the brazed specimens are presented graphically in figure II-24.

The data from the 48Zr-48Ti-4Be system with alumina ceramic indicate that the predetermined brazing temperature (1940° F) and the standard brazing schedule (five-minute hold at the brazing temperature) is near optimum. No appreciable increase in strength was noted as a function of increasing brazing time or temperature. A sharp decrease in the wetting angle was noted at the higher temperatures. Previous work (ref. II-1) had shown that shorter hold times and lower brazing temperatures resulted in incomplete melting of the alloy.

Microstructures of sections from the 48Zr-48Ti-4Be test specimens brazed at the "zero" hold time (1 to 5 seconds at 1940° F), standard schedule (5 minutes at 1940° F), and "BT+180° F" (2120° F, 5-minute hold) were examined (figure II-25). These represent the range of the diffusion conditions evaluated. The samples showed extensive reaction with the alumina ceramic. Particles of alumina had been carried into the melt phase in all three cases, although the erosion was very small in the first ("zero hold") case.

The eutectic phase was much more extensive in the "BT+180° F" sample. This was caused by increased reaction with the metal member. The thick reaction zone on the side of the Cb-1Zr metal member is indicative of the degree of reaction. In such systems, with phases that solidify out at higher temperatures, a certain minimal amount of the more ductile eutectic phase is desirable to insure against voids, cracks and possible vacuum leaks on cooling. This consideration also indicates that a slightly higher brazing temperature (~65° F) than the predetermined tempera-

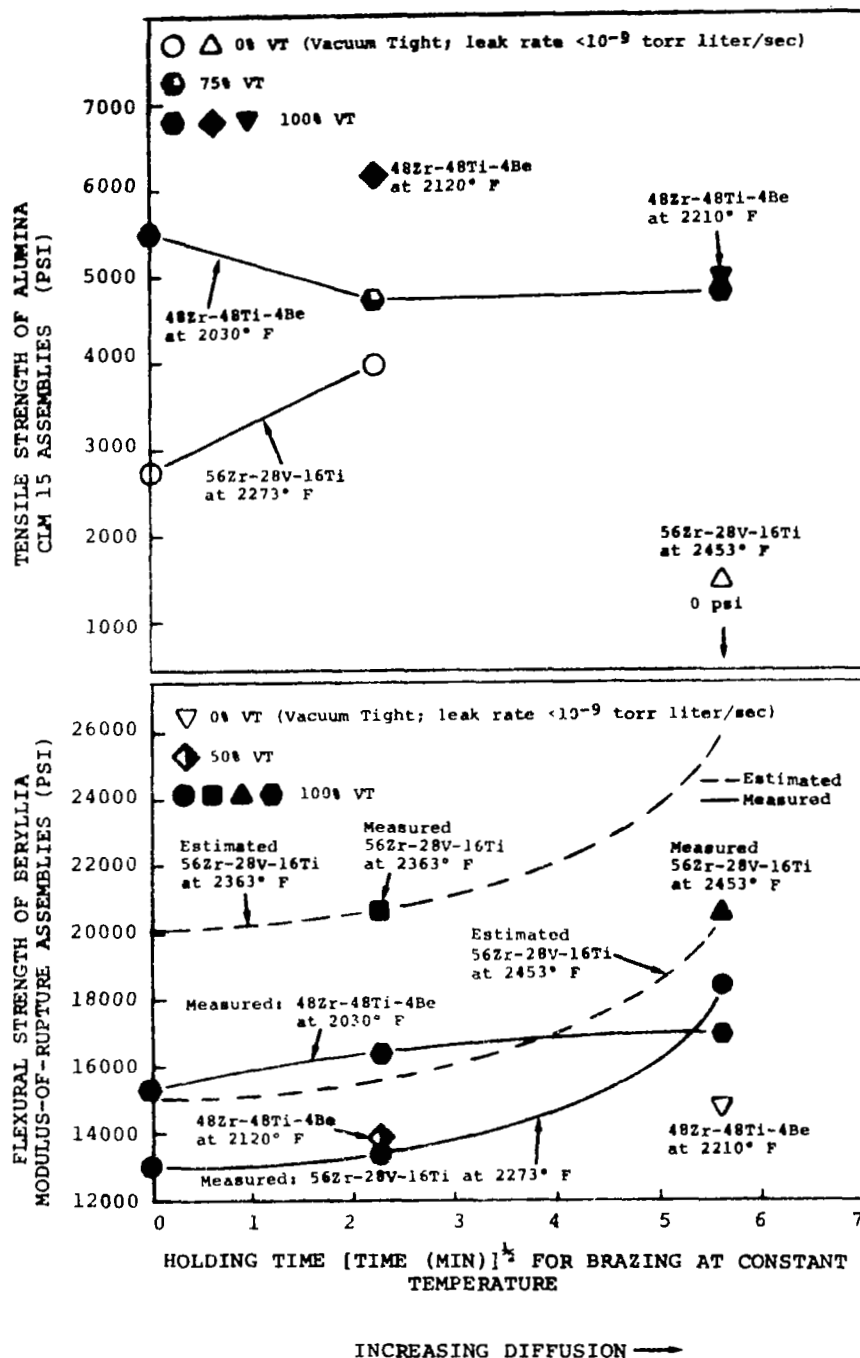


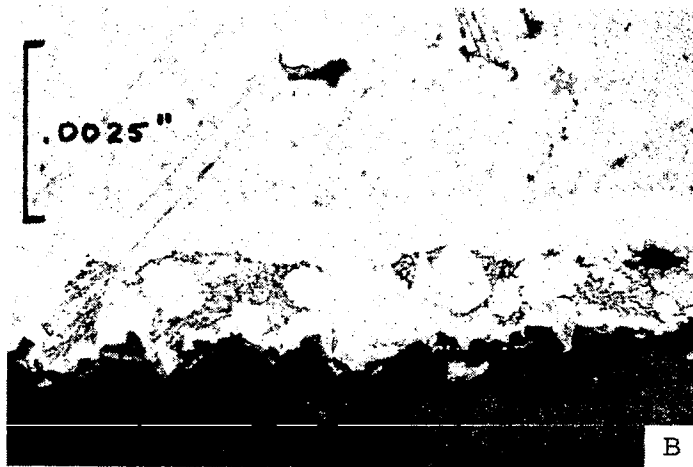
FIGURE II-24. Effect of Increasing Diffusion on the Strength and Vacuum Integrity of Alumina-(Cb-1Zr) and Beryllia-(Cb-1Zr) Systems Brazed with Alloys 48Zr-48Ti-4Be or 56Zr-28V-16Ti



Cb-1Zr

Braze 48Zr-48Ti-4Be  
at 1940°F, zero hold time

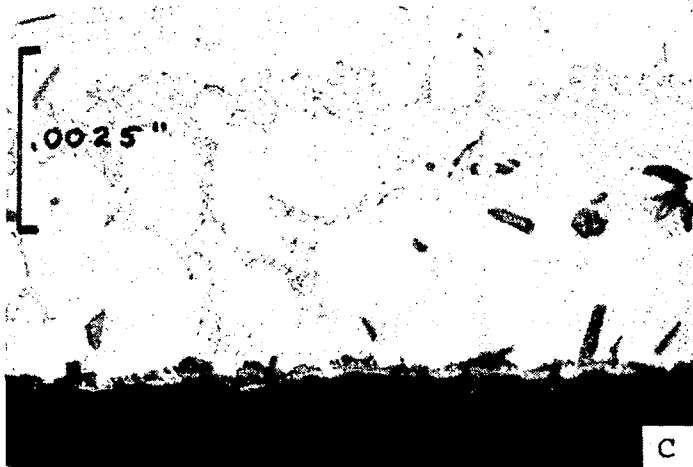
99.8% Al<sub>2</sub>O<sub>3</sub>



Cb-1Zr

Braze 48Zr-48Ti-4Be  
at 1940°F, 5 minute hold  
time

99.8% Al<sub>2</sub>O<sub>3</sub>



Cb-1Zr

Braze 48Zr-48Ti-4Be  
at 2120°F, 5 minute hold  
time

99.8% Al<sub>2</sub>O<sub>3</sub>

Void

Etchant: 30 ml lactic acid, 10 ml HNO<sub>3</sub>, 10 ml HF

FIGURE II-25. Photomicrographs of the 99.8% Al<sub>2</sub>O<sub>3</sub>/48Zr-48Ti-4Be/Cb-1Zr Seal Systems After Various Brazing Conditions 400X

ature would be beneficial. The increased reaction with the columbium-1% zirconium gave a very thick brazed joint in the "BT+180° F" sample. This confirms the conclusion from the strength data that the temperature should be raised much less than 180° F.

The tests on 99.7% alumina ceramic with 56Zr-28V-16Ti brazing alloy produced a low yield of vacuum tight assemblies. This brazing alloy is evidently marginal with alumina even at the lower brazing temperature because of its reactivity with alumina. Micrographs of samples bracketing the diffusion treatment conditions support the above reasoning (figure II-26). The reaction at the brazement-alumina interface at the lower temperature resulted in round inclusions of alumina being carried into the melt phase. In the "BT+180° F" sample the reaction resulted in the complete dissolution of alumina grains.

Upon consideration of the strength data and interpretation of the photomicrographs, this alloy is not recommended for use with alumina. It is possible that a diffusion layer of molybdenum or columbium could be placed on the alumina before brazing to reduce the reactivity locally during brazing.

Data from the brazing tests of these two alloys with beryllia ceramic indicate that the standard brazing temperature for the 48Zr-48Ti-4Be alloy is near optimum, but the hold time is flexible. The production of vacuum tight assemblies with this alloy shows the expected greater stability of beryllia over alumina ceramic.

The data for brazing alloy 56Zr-28V-16Ti show that the standard brazing cycle was not optimum with BeO, but appears to have substantial flexibility. The degree of wetting with this alloy appears to be nearly independent of the brazing conditions. As a result of these tests, the standard cycle was revised to 2436° F (BT+60° F) with a 5-minute hold. The encouraging results with 56Zr-28V-16Ti/BeO made this combination remain a primary candidate for bore seal development. Its superiority to 48Zr-48Ti-4Be when joining to BeO is readily apparent from figure II-24, so the latter alloy was eliminated from further consideration. In addition, 48Zr-48Ti-4Be is too reactive with alumina ceramics.

Gb-1Zr

Braze 56Zr-28V-16Ti at  
2273°F, zero hold time

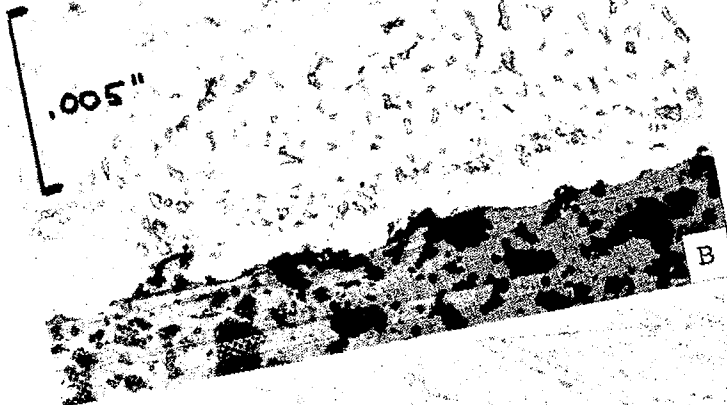


Void

99.8% Al<sub>2</sub>O<sub>3</sub>

Gb-1Zr

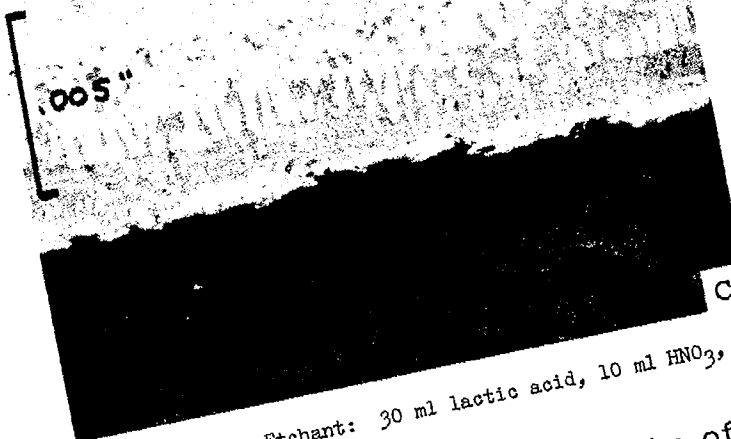
Braze 56Zr-28V-16Ti at  
2273°F, 5 minute hold time



99.8% Al<sub>2</sub>O<sub>3</sub>

Gb-1Zr

Braze 56Zr-28V-16Ti at  
2453°F, 5 minute hold time



Void

99.8% Al<sub>2</sub>O<sub>3</sub>

Etchant: 30 ml lactic acid, 10 ml HNO<sub>3</sub>, 10 ml HF

Micrographs of the 99.8% Al<sub>2</sub>O<sub>3</sub>/  
Gb-1Zr Seal Systems  
Conditions 400X



Thermalox 998 (99.8% BeO) test specimens were brazed with the 60Zr-25V-15Cb alloy at the predetermined brazing temperature (2436° F) and at 90° F higher, 180° F higher and 108° F lower. The hold time was five minutes. Brazements at all brazing temperatures showed good filleting but those held at the highest temperature were not superior to those obtained at 2526° and 2436° F. The data are shown in table II-17. These data indicate that all joints brazed between 2328° and 2526° F were stronger than the ceramic as all breaks occurred in the ceramic. Since higher strength was obtained with the specimens brazed at the higher temperatures, a possible heat-treatment effect on the beryllia ceramic was being manifested. The same trend was noted with beryllia bars tested in the as-received condition and after 500 hours exposure to vacuum at 1600° F. The joints which were brazed at 2616° F were weaker than the ceramic as shown by the modulus-of-rupture values and the fact that the fractures were all located at the ceramic-brazement interface.

It was concluded that the 2436° F standard brazing temperature was suitable for initial attempts to braze larger seals and that a substantial range of temperatures was available within which good seals could be made.

(4) Selection of Brazed Systems for Alkali Metal Exposure Tests and for Construction of Four-Inch Model Bore Seals

The application of an evaporated wetting layer of molybdenum on the ceramic member improved the strength and vacuum integrity of ceramic-to-metal seals. These processing improvements were applied to the alloy systems which were selected for further evaluation.

From the six brazing alloys discussed previously, the following were selected for 500-hour, 1600° F tests in potassium:

BeO\* (68Ti-28V-4Be) Cb-1Zr;  
Brazing Temperature: 2372° F  
Brazing Time: 5 minutes

BeO (46Zr-46Ti-4Be) Cb-1Zr;  
Brazing Temperature: 1832° F  
Brazing Time: 5 minutes

BeO\* (60Zr-25V-15Cb) Cb-1Zr;  
Brazing Temperature: 2436° F  
Brazing Time: 5 minutes

The beryllia ceramic in the systems marked with an asterisk (\*) were coated with a 1 $\mu$ -to 3 $\mu$ -thick layer of molybdenum by the evaporation metallizing process (See Appendix A, MP-1) before brazing.

##### 5. Ceramic Outgassing Study

Alumina and beryllia ceramics are normally fabricated by sintering the appropriate compacted powders in an oxidizing atmosphere for 1/2 to 3 hours at temperatures in the 2700° to 3100° F (1500° to 1700° C) range. Dissolved, chemisorbed and occluded oxygen-containing gases (H<sub>2</sub>O, CO, CO<sub>2</sub>) are therefore released by the ceramics during subsequent treatment or use at elevated temperatures. The availability or presence of oxygen in alkali-metal accelerates its corrosive effect toward refractory metals. The purpose of this study was to determine the species and amount of gaseous oxygen compounds remaining in selected bore seal ceramics (wall thickness 0.040 to 0.100 inch) after various processing schedules, as measured by vacuum outgassing at proposed operating temperatures for bore seals. Corrective action such as prolonged high temperature vacuum firing could be programmed if shown necessary by this study.

The residual bulk outgassing rates of similarly fabricated and sintered ceramics should be similar. For this reason, three materials were selected to represent different fabricating and sintering procedures:

- a) Sapphire, single crystal ~100 percent alumina; flame fusion grown in an oxy-acetylene flame; no grain boundaries, no apparent voids, density 3.98 g/cc.
- b) Lucalox, polycrystalline 99.8 percent alumina, -0.2 percent magnesia; sintered in hydrogen; with grain boundaries, but almost no voids; essentially 100 percent theoretical density, 3.98 g/cc.
- c) Thermalox 998, polycrystalline 99.8 percent beryllia; sintered in air atmosphere electric kiln; with grain boundaries and voids; 95 to 98 percent theoretical density, 2.86 - 2.95 g/cc.

The beryllia and alumina were representative bore seal ceramics and the sapphire was a control which would give an indication of the importance of grain boundaries and voids to residual

outgassing. These three materials were sintered in different atmospheres.

Two outgassing temperatures and three different sample preparations were selected for the study. The two temperatures were 1000° and 1600° F. The three preconditioning treatments were:

Precondition 1 (PC1): After dye check and ceramic cleaning procedures. (See Appendix A, MP-1).

Precondition 2 (PC2): After dye check and ceramic cleaning procedures plus 10 minutes at 1832° F (1000° C) at a pressure of less than  $5 \times 10^{-6}$  torr.

Precondition 3 (PC3): After dye check and ceramic cleaning procedures plus 30 minutes at 2597° F (1425° C) in 75%N<sub>2</sub>-25%H<sub>2</sub> with 100° F dew point, plus 10 minutes at 1832° F (1000° C) at a pressure of less than  $5 \times 10^{-6}$  torr.

The specific sample preparation and test distribution are shown in table II-9. The 1832° F vacuum firing and the 2597° F firing in 75%N<sub>2</sub>-25%H<sub>2</sub> gas mixture were routine firings given to all ceramics on this program prior to vacuum brazing.

The sample surface areas and weights are given in table II-10. Trial runs were made to determine the sample size that would give a gas evolution rate which could be handled by the 1.0 l/sec pumping speed of the system.

Composition of the firing gases is given in table II-11. The ram furnace is reserved for BeO because of its toxic properties. Although inlet gas to the two furnaces is identical, CO is formed in the tunnel furnace because of reaction of water vapor with the continuous line of carbon boats used to hold the parts.

Curves of total pressure and partial pressure of gases with mass-to-charge ratios of 2, 18, 28, and 44 were obtained as a function of time and are shown in figures II-27 to II-37. The total evolved gas  $Q_T$  in units of  $10^{-4}$  torr-liters/gram-sec was obtained from specimens having surface areas and weights as given in table II-10.

TABLE II-9. Test Distribution for Ceramic Outgassing Measurements

Ceramic	Nominal Composition	Outgassing Test Temperature	Ceramic Precondition			
			(a) As Received	(b) Vacuum Fired	(c) Clean and Vacuum Fired	(d) Clean and Vacuum Fired
Sapphire (Linde)	Single Crystal 100% $\text{Al}_2\text{O}_3$ , Essentially Zero Porosity	1000°F 1600°F	X X	X X	X X	X
Lucalox (G. E.)	Sintered 99.8% $\text{Al}_2\text{O}_3$ , Essentially Zero Porosity	1000°F 1600°F	X	X	X X	X X
Thermalox 998 (Brush)	Sintered 99.8% BeO 2-5% Porosity	1000°F 1600°F	X	X	X X	X X

(a) - Precondition 1. After dye check and ceramic cleaning procedures (see Appendix A).  
 (b) - Precondition 2. Dye check and ceramic cleaning plus 10 minutes at 1832 F at less than  $5 \times 10^{-6}$  torr.  
 (c) - Precondition 3. Dye check plus ceramic cleaning plus 30 minute fire at 2597°F in 75%  $\text{N}_2$ -25%  $\text{H}_2$ ; 100°F dew point plus 10 minutes at 1832 F at  $5 \times 10^{-6}$  torr.  
 (d) - As in (c) above except 120 minutes vacuum fire at 2192°F at less than  $5 \times 10^{-6}$  torr.

TABLE II-10. Ceramic Outgassing Samples, Weights, Surface Areas, and Gas Quantities (torr-liters/g) at 1000° and 1600°F

Sample	1000° F for 20 minutes			1600° F for 20 minutes		
	Weight (grams)	Area ( $\text{Cm}^2$ )	Gas Evolved $Q_T$	Weight (grams)	Area ( $\text{Cm}^2$ )	Gas Evolved $Q_T$
Sapphire, 100% $\text{Al}_2\text{O}_3$ (0.10 inch Round Rod)						
Precondition 1 (a)	0.2646	1.16	$40 \times 10^{-4}$ torr-liter/g	0.2644	1.16	$54 \times 10^{-4}$ torr-liter/g
Precondition 2 (b)	0.2497	1.12	$511 \times 10^{-4}$ torr-liter/g	0.2697	1.17	$20 \times 10^{-4}$ torr-liter/g
Precondition 3 (c)	0.2637	1.06	$3.5 \times 10^{-4}$ torr-liter/g	0.2641	1.07	$6 \times 10^{-4}$ torr-liter/g
Lucalox (99.8% $\text{Al}_2\text{O}_3$ ) (0.10 inch Square Rod)						
Precondition 1				0.3764	1.69	$40 \times 10^{-4}$ torr-liter/g
Precondition 2				0.3404	1.59	$18 \times 10^{-4}$ torr-liter/g
Precondition 3				0.3764	1.69	$10 \times 10^{-4}$ torr-liter/g
Thermalox 998, (99.8% BeO) (0.10 inch Square Rod)						
Precondition 1				0.3450	1.99	$47 \times 10^{-4}$ torr-liter/g
Precondition 2				0.3567	1.99	$13 \times 10^{-4}$ torr-liter/g
Precondition 3	0.3328	1.88	$4 \times 10^{-4}$ torr-liter/g	0.3495	2.19	$10 \times 10^{-4}$ torr-liter/g

Notes: (a) Precondition 1 - after dye check and ceramic cleaning procedures  
 (b) Precondition 2 - after dye check, ceramic cleaning and vacuum firing 10 minutes at 1832 F at less than  $5 \times 10^{-6}$  torr  
 (c) Precondition 3 - after dye check, ceramic cleaning plus 30 minutes firing at 2597°F in 75%  $\text{N}_2$ -25%  $\text{H}_2$  with 100°F dew point, followed by vacuum firing at 1832°F for 10 minutes at less than  $5 \times 10^{-6}$  torr.

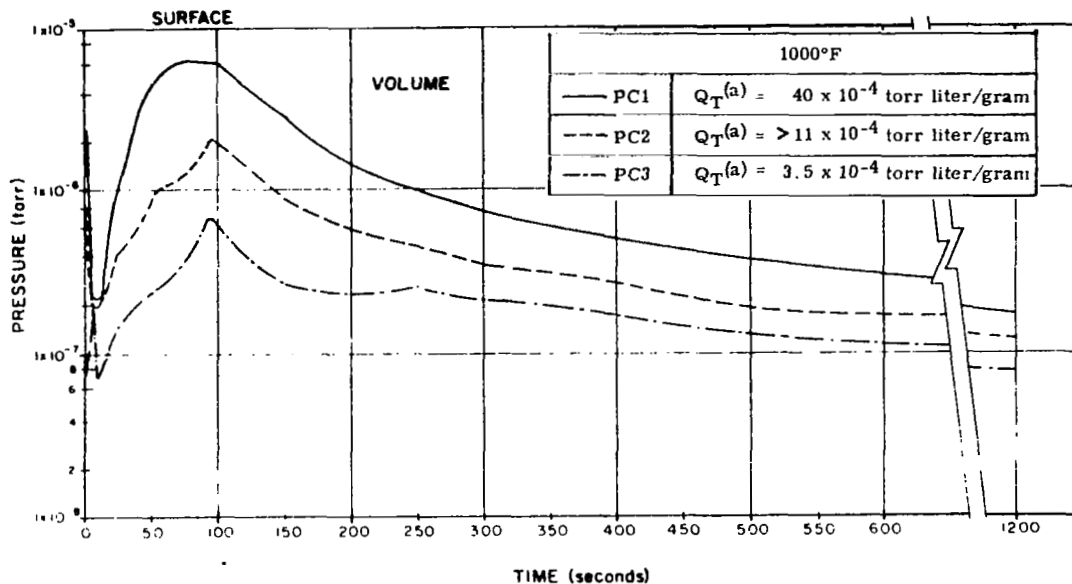
TABLE II-11. Typical Compositions of Nitrogen-Hydrogen Gas Atmospheres in Furnace Hot Zone During 2597°F Firing of Ceramics (a)

Furnace	Gas Composition <sup>(b)</sup> (Volume Percent)			
	Nitrogen (N <sub>2</sub> )	Carbon Monoxide (CO)	Argon plus Oxygen (A + O <sub>2</sub> )	Hydrogen (H)
Tunnel Furnace	71.13	3.02	0.85	balance
Ram Furnace	74.68	0	0.31	balance
<p>(a) Alumina parts are fired in a tunnel furnace and the beryllia parts in a ram furnace.</p> <p>(b) Averaged from data obtained with Burrell KROMO-TOG Model #K2 gas chromatograph.</p>				

In the total pressure curves, the first sharp peak is interpreted as surface gas disturbed by sliding the sample into the furnace. The second peak, in most cases nearly obliterated by the volume peak, is caused by loss of surface gas. These occur within the first minute of testing.

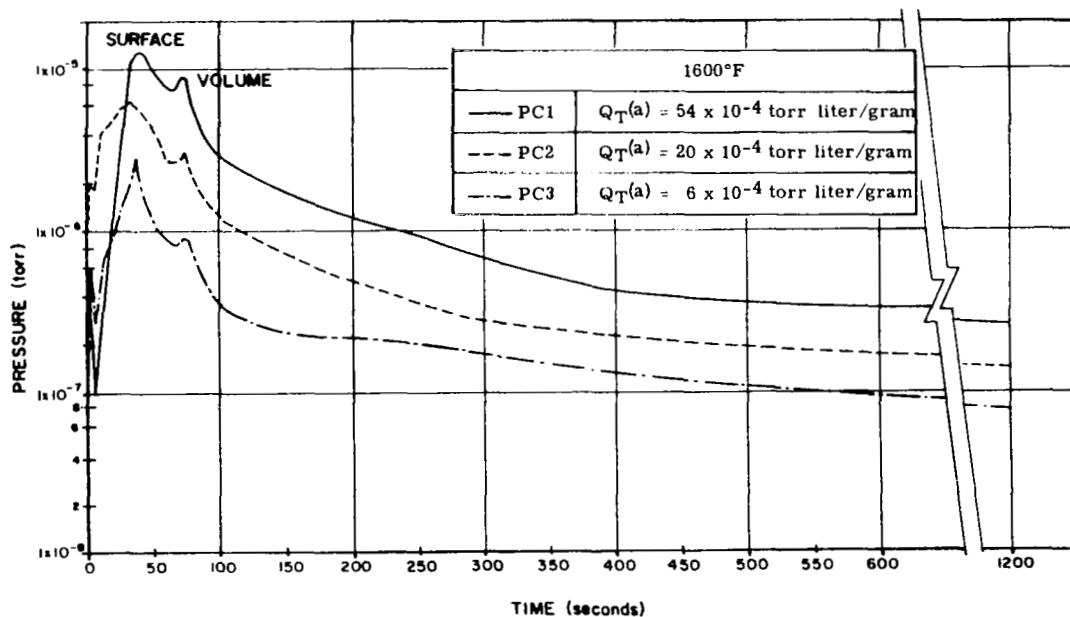
The partial pressures of selected gases as well as the total pressure were monitored on each outgassing run. The four specific gases monitored were hydrogen (H, m/e = 2), water vapor (H<sub>2</sub>O, m/e = 18), nitrogen and/or carbon monoxide (N<sub>2</sub>, m/e = 28; CO, m/e = 28) and carbon dioxide (CO<sub>2</sub>, m/e = 44). These gases accounted for nearly all gas evolved since the partial pressures add to within a few percent of the total pressure. Methane (CH<sub>4</sub>, m/e = 16) was not monitored specifically, although it was always measured due to its proximity to water vapor, m/e = 18, which was monitored.

The partial pressure curves obtained from the raw data have been smoothed out and the remaining inflections are considered real and significant. For example, deviations from the normal uniform decay in pressure are noted, such as the hydrogen peaks (m/e = 2) at 4 minutes on the Thermalox 998, in precondition 3 on the (figures II-34 and II-37) 1000° and 1600° F curves. Starting background levels for the individual gaseous components, just prior to sample drop, are noted on the left hand margins of the figures and by faint lines extending horizontally across the figures.



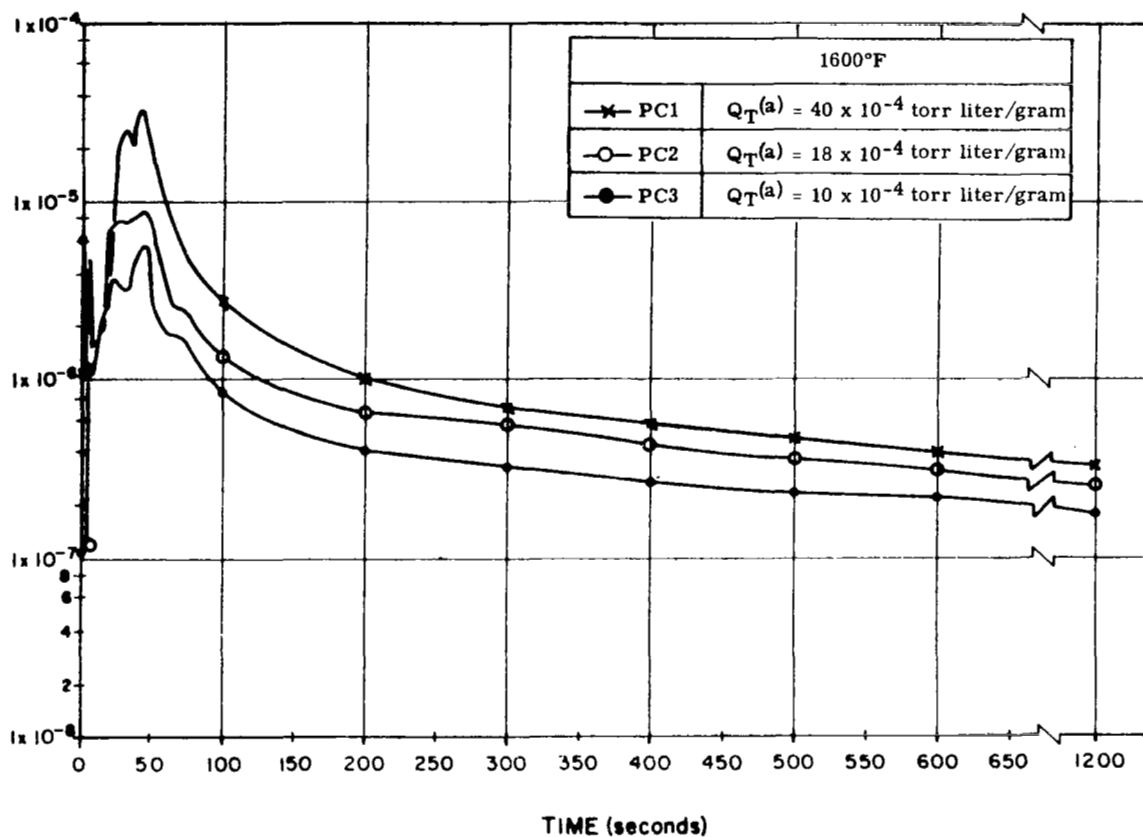
(a) Adjusted for calibrated pumping speed on the vacuum furnace

FIGURE II-27. Total(a) Pressure Outgassing Curves at 1000°F Furnace Temperature for Sapphire (100%Al<sub>2</sub>O<sub>3</sub>, density 3.98 g/cc) Samples for Preconditions 1, 2, and 3



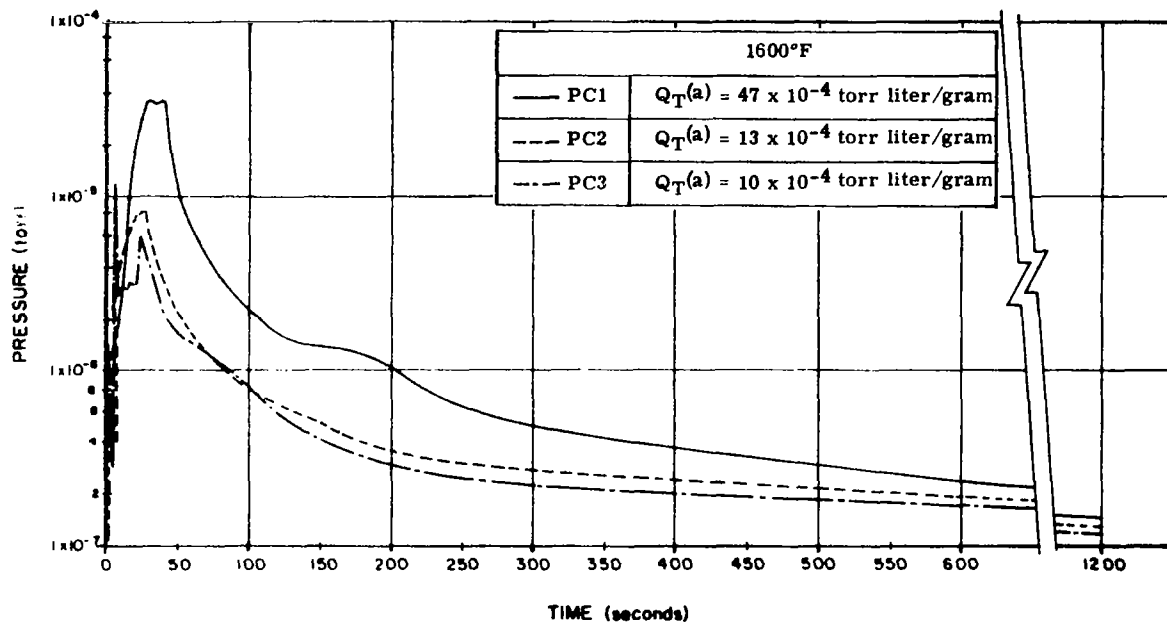
(a) Adjusted for calibrated pumping speed on the vacuum furnace

FIGURE II-28. Total(a) Pressure Outgassing Curves at 1600°F Furnace Temperature for Sapphire (100%Al<sub>2</sub>O<sub>3</sub>, density 3.98 g/cc) Samples with Preconditions 1, 2, and 3



(a) Adjusted for calibrated pumping speed on the vacuum furnace

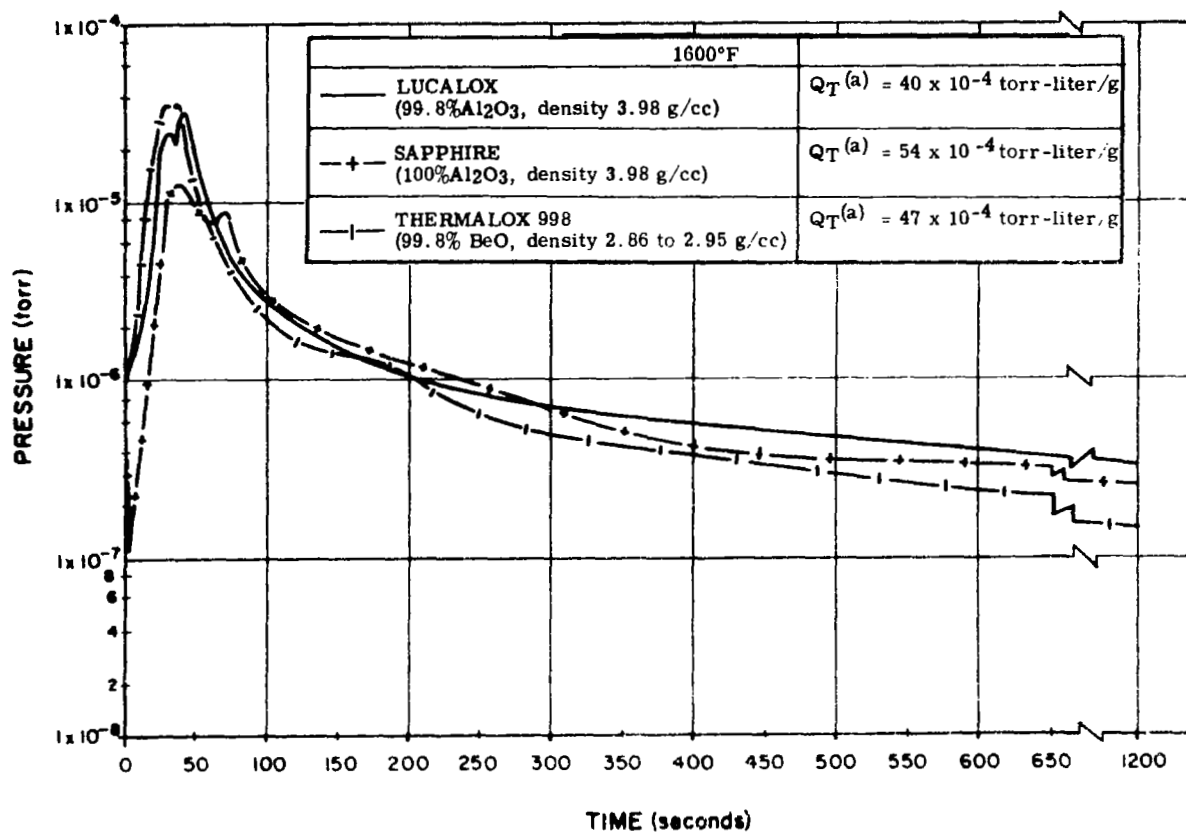
FIGURE II-29. Total(a) Pressure Outgassing Curves at 1600°F  
Furnace Temperature for Lucalox (99.8%Al<sub>2</sub>O<sub>3</sub>,  
density 3.98 g/cc) Samples for Preconditions  
1, 2, and 3



(a) Adjusted for calibrated pumping speed on the vacuum furnace

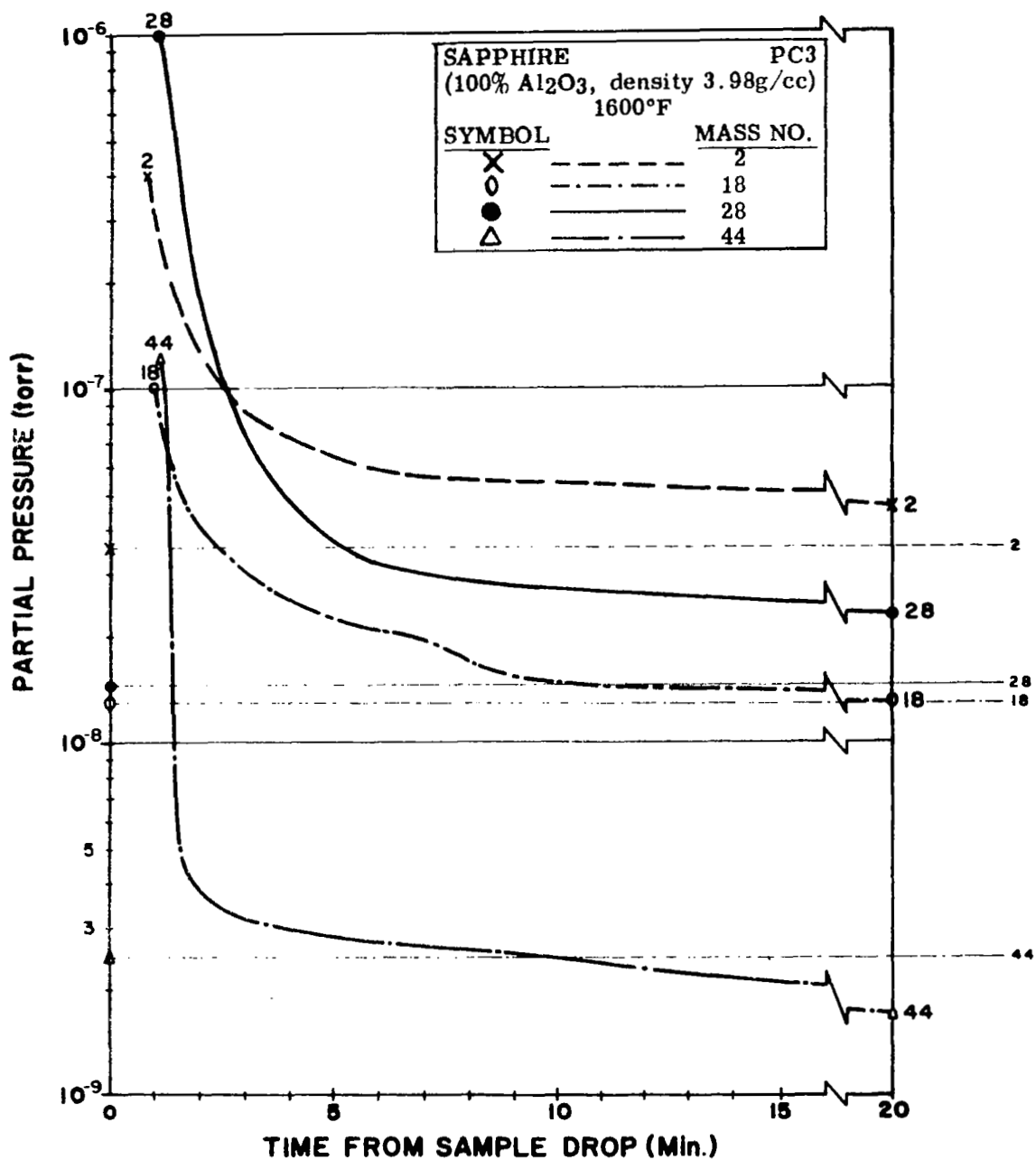
FIGURE II-30. Total(a) Pressure Outgassing Curves at 1600°F  
Furnace Temperature for Thermalox 998 (99.8%  
BeO, density 2.86 to 2.98 g/cc) Samples for  
Preconditions 1, 2, and 3





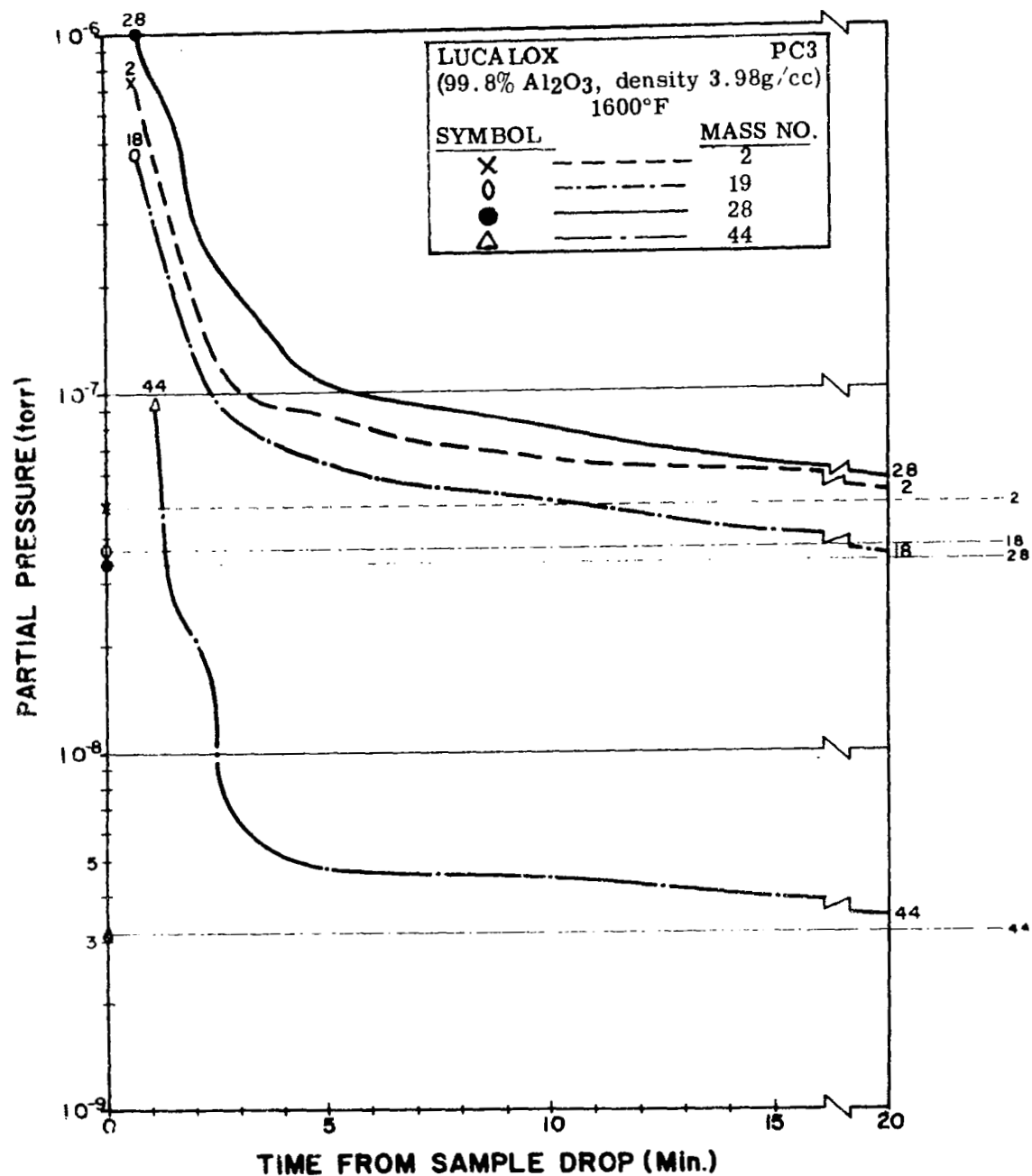
(a) Adjusted for calibrated pumping speed on the vacuum furnace

FIGURE II-31. Total (a) Pressure Outgassing Curves at 1600°F for Sapphire, Lucalox, and Thermalox 998 After Dye Check and Ceramic Cleaning Procedures (PC1)



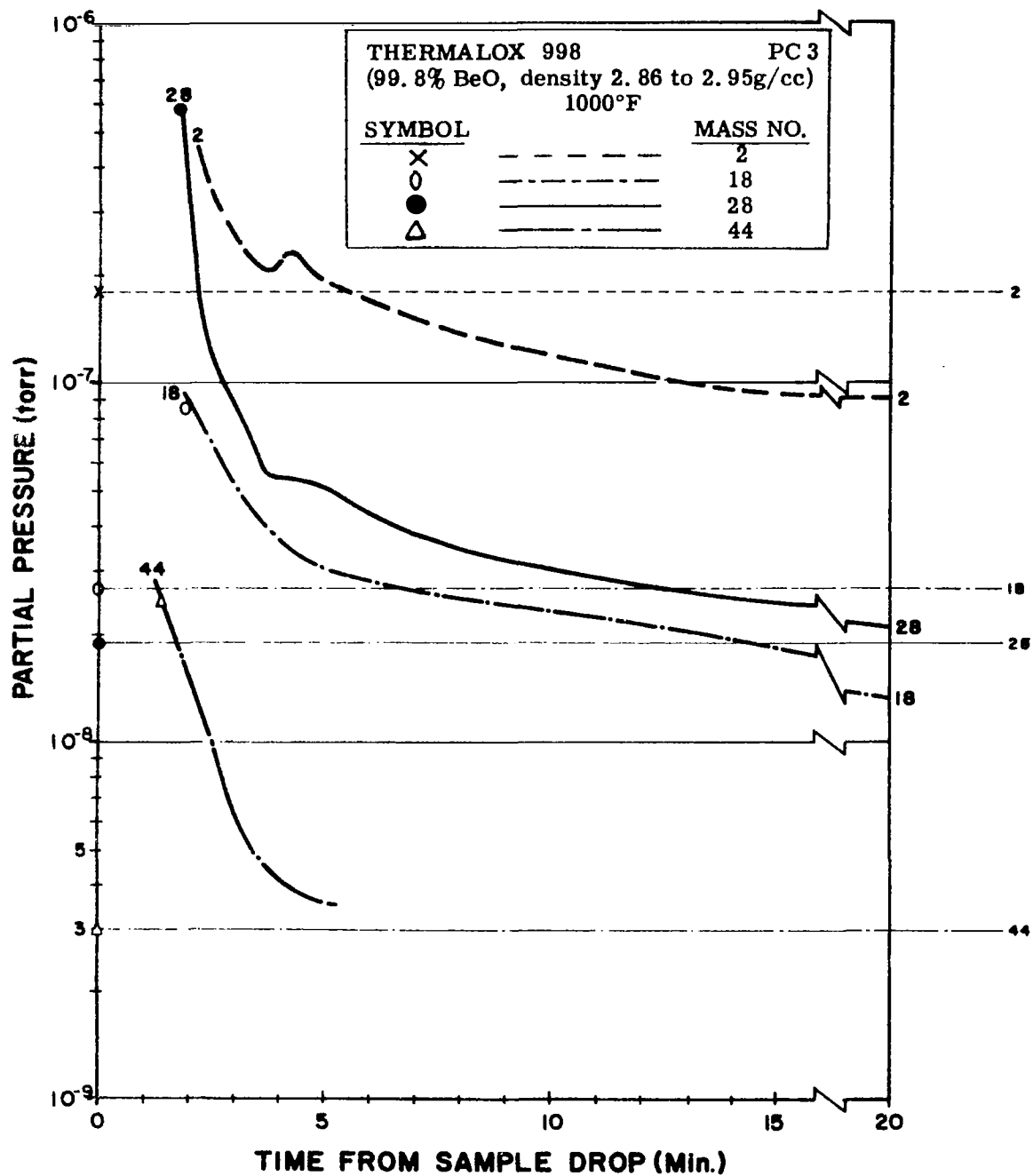
Horizontal lines indicate the furnace background pressure for the gas with the designated mass number.

FIGURE II-32. Partial Pressure Curves of Outgassed Products For Sapphire (100% $\text{Al}_2\text{O}_3$ , density 3.98 g/cc) Precondition 3, Outgassed at 1600°F



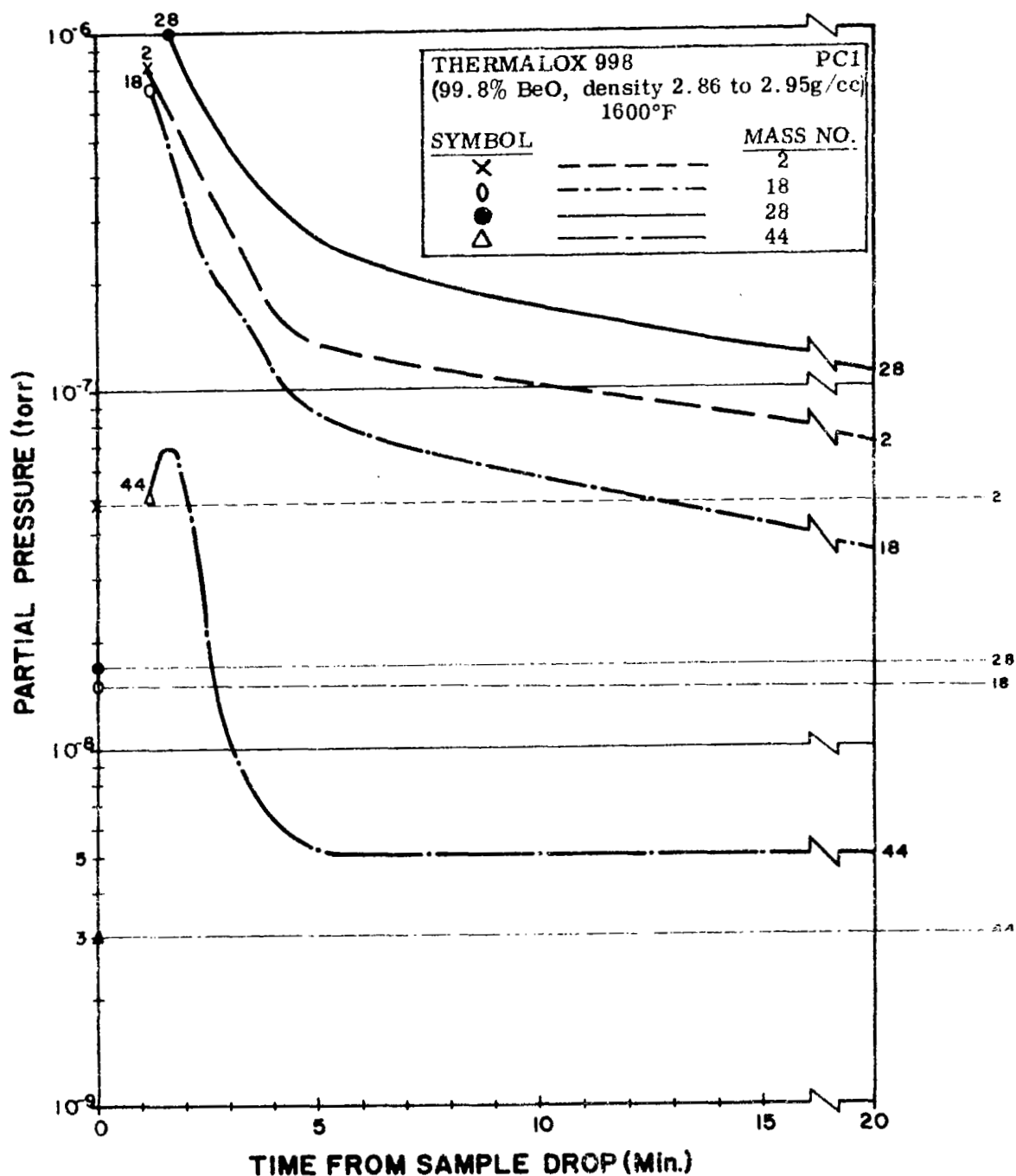
Horizontal lines indicate the furnace background pressure for the gas with the designated mass number

FIGURE II-33. Partial Pressure Curves of Outgassed Products for Lucalox (99.8% $\text{Al}_2\text{O}_3$ , density 3.98 g/cc) with Pre-condition 3, Outgassed at 1600°F



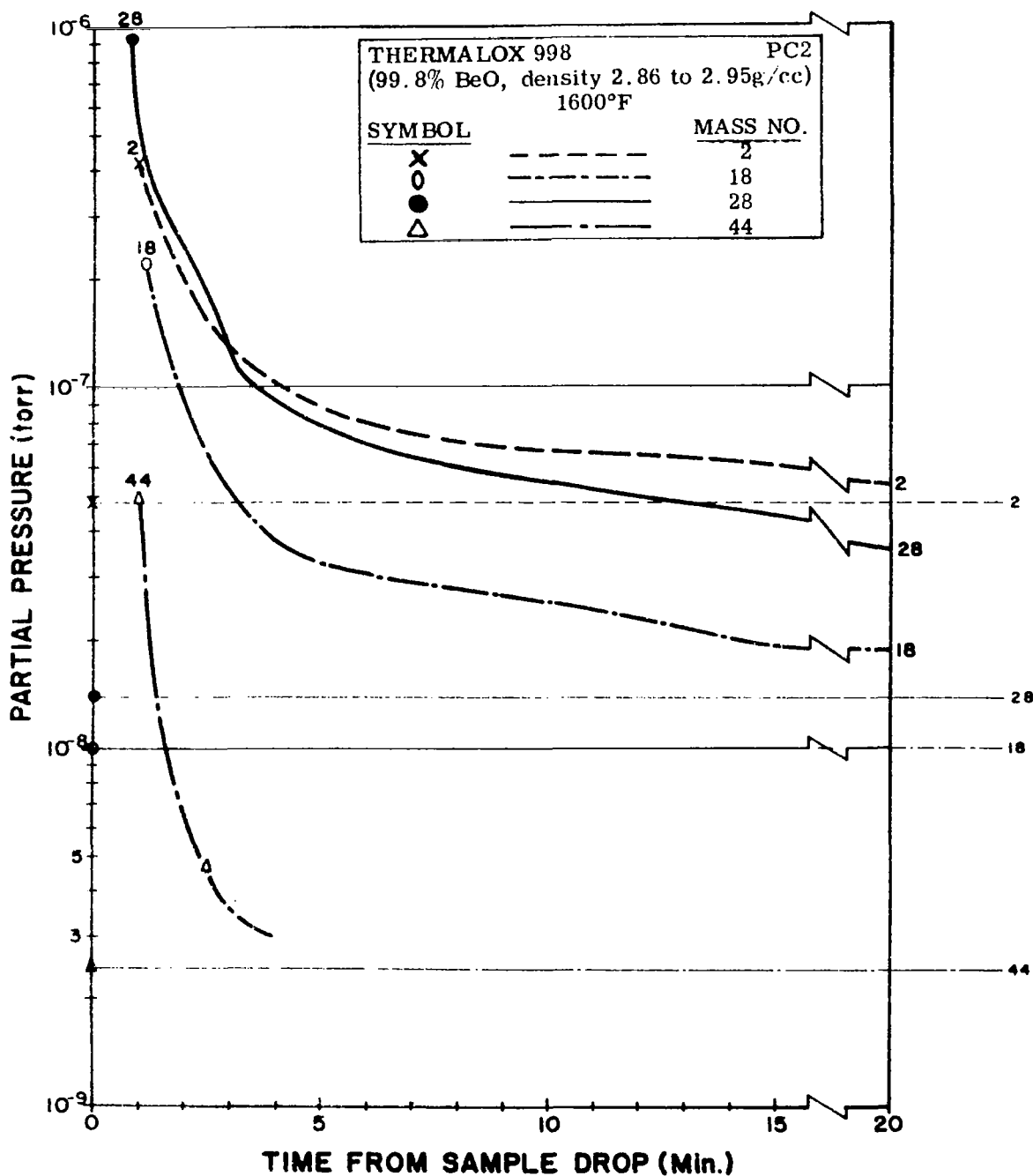
Horizontal lines indicate the furnace background pressure for the gas with the designated mass number.

FIGURE II-34. Partial Pressure Curves of Outgassed Products for Thermalox 998 (99.8%BeO, density 2.86 to 2.95 g/cc) Precondition 3, Outgassed at 1000°F



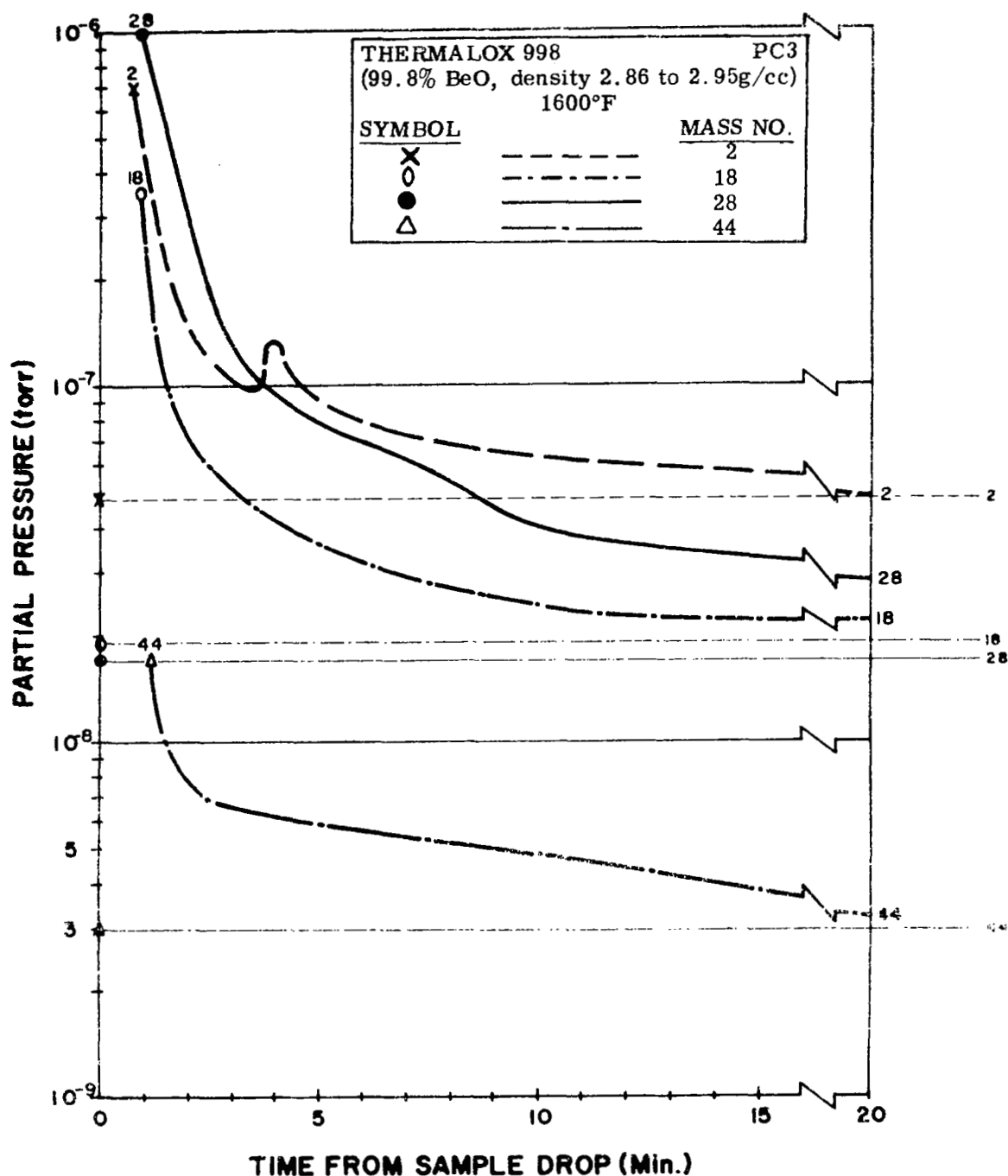
Horizontal lines indicate the furnace background pressure for the gas with the designated mass number.

FIGURE II-35. Partial Pressure Curves of Outgassed Products for Thermalox 998 (99.8%BeO, density 2.86 to 2.95 g/cc) with Precondition 1, Outgassed at 1600°F



Horizontal lines indicate the furnace background pressure for the gas with the designated mass number.

FIGURE II-36. Partial Pressure Curves of Outgassed Products for Thermalox 998 (99.8%BeO, density 2.86 to 2.95 g/cc) with Precondition 2, Outgassed at 1600°F



Horizontal lines indicate the furnace background pressure for the gas with the designated mass number.

FIGURE II-37. Partial Pressure Curves of Outgassed Products for Thermalox 998 (99.8%BeO, density 2.86 to 2.95 g/cc) with Precondition 3, Outgassed at 1600°F

Table II-10 shows that in all cases the total evolved gas from dye checked and cleaned ceramic (precondition 1) was significantly reduced by vacuum firing (precondition 2) and was reduced further when the vacuum firing was preceded by firing the samples at high temperature ( $\sim 2600^\circ \text{F}$ ) in 75% $\text{N}_2$ -25% $\text{H}_2$  forming gas (precondition 3). The partial pressure curves (figures II-32, II-33, and II-37) show that after 20 minutes of outgassing at  $1600^\circ \text{F}$ , all three materials in the precondition 3 form indicate pressures within  $2 \times 10^{-8}$  torr of the furnace background pressure for each of the four monitored mass-to-charge ratios. An extrapolation of these curves shows that after an additional 20 minutes the partial pressures would fall below the corresponding starting pressures in all cases.

The most significant gases remaining after 20 minutes outgassing at  $1600^\circ \text{F}$  in all materials in precondition 3 are those with  $m/e = 28$ . The water vapor ( $m/e = 18$ ) is essentially down to background level and the hydrogen ( $m/e = 2$ ) is of lesser importance since it is not a liquid alkali metal corrosion accelerator. As stated previously,  $m/e = 28$  represents nitrogen and/or carbon monoxide. To resolve the question of the ratio of nitrogen to carbon monoxide, it is necessary to measure other secondary  $m/e$  partial pressures which are over an order of magnitude less intense and are therefore at the sensitivity limit of the equipment used. As a result, only qualitative results were possible and these indicated a CO to  $\text{N}_2$  ratio of approximately 7 to 1.

The  $m/e$  ratios of 14, 16, 18, and 28 after 30 minutes (or for the longest period for each determination) were measured for each determination. In all cases the  $m/e = 16$  peak ( $\text{O}$  or  $\text{CH}_4$ ) was greater than could be accounted for by the  $\text{H}_2\text{O}$ ,  $m/e = 18$  and  $\text{N}_2$  or  $\text{CO}$ ,  $m/e = 28$  peaks, which implied that the balance of the peak was due to methane ( $\text{CH}_4$ ,  $m/e = 16$ ). This was confirmed by the fact that Lucalox emitted less methane than did sapphire. Since Lucalox is hydrogen sintered while sapphire is grown in an acetylene heated atmosphere, the deduction is reasonable.

The outgassing data indicate that each gram of sapphire, Lucalox or Thermalox 998, which are given the treatment described as precondition 3 and outgassed at  $1600^\circ \text{F}$  for 20 minutes, will evolve approximately  $30\mu\text{g}$  of oxygen (as CO) during the following 20 minutes at  $1600^\circ \text{F}$ . If on the other hand, the evolved gas during the second 20 minutes is assumed to consist entirely of nitrogen, then approximately  $80\mu\text{g}$  will be released from each gram of ceramic.



The evolved gases have been reported in units of gas per unit of weight for the ceramics, since it is believed that the bulk gases are of more importance than the surface gases. The latter can be removed from a completed structure with a relatively simple bakeout.

If the mass of the ceramic in a space electric power system were equal in weight to the mass of the alkali metal, the liquid alkali metal would be contaminated with 30 ppm oxygen or 80 ppm nitrogen assuming the worst case for potassium and lithium respectively (e.g., 30 $\mu$ g oxygen per gram of ceramic transferred into each gram of alkali metal equals 30 ppm contamination). Since practical systems may contain at least 10 times the mass of alkali metal than they do of ceramic, the contamination is reduced to less than 3 ppm and 8 ppm respectively. For small tests such as capsule tests the ceramic-to-alkali metal weight ratio is such that contamination is possible without adequate bakeout and handling and increases the possibility of contamination. Therefore, the present ceramic preparation procedure of dye checking, ceramic cleaning (in detergent) and clean firing at 2597° F in 75%N<sub>2</sub>-25%H<sub>2</sub> is adequate if the processing precautions outlined below are followed.

The vacuum brazing operation (which was of longer duration and takes place at higher temperature than the 10 minutes at 1832° F applied in the outgassing study) was adequate as a vacuum firing step without a prior vacuum firing. A prior vacuum firing was useful only insofar as it permitted the vacuum brazing operation to be carried out more rapidly.

Completed brazed assemblies should be stored in clean polyethylene bags. Handling with bare hands should not be permitted. If handling, which contaminates the ceramic, is necessary, it will prolong the vacuum firing of the completed system which must be carried out before the introduction of alkali metal into that system.

The completed system (loop, generator, etc.) should be vacuum outgassed at the operating temperature (1600° F in the case cited) for the time required to get the system pressure down to well below 5x10<sup>-6</sup> torr before introducing alkali metal.

## 6. Alkali-Metal Exposure Tests

Since bore seals will be required to operate for long periods of time in vacuum and an alkali-metal vapor (probably potassium) environment, 2000-hour static alkali-metal exposure tests were conducted. Candidate ceramics and ceramic-to-metal seal systems, which showed promise after 500-hour exposure at 1000° and 1600° F in previous tests (ref. II-1), were scheduled for 2000-hour tests in alkali-metal vapor at 1600° F on this pro-

gram. Concurrent tests at 1600° F in vacuum were also scheduled to determine the effect of temperature in vacuum. In addition, improved sealing systems that had been developed (and proof tested during 500-hour alkali-metal tests at 1600° F) on this program were also scheduled for the 2000-hour alkali-metal and vacuum tests. During the course of this program a ceramic-to-metal seal system was scaled-up from test specimen size to a 4-inch diameter model bore seal. There was some uncertainty regarding the impurity level and porosity of the 4-inch diameter beryllia ceramic tubes that had been fabricated for making the model bore seal capsules. Therefore, one 4-inch diameter bore seal capsule was sectioned to provide modulus-of-rupture bars which were also subjected to 500-hour alkali-metal exposure tests at 1600° F in columbium-1% zirconium test capsules.

The fabrication of the static Cb-1Zr test capsules used in the alkali-metal tests was described in Section II-B.1. The facility for loading test capsules, the alkali-metal loading procedure, and test capsule closure were also described in Section II-B.1.

A description of the vacuum furnace used in the elevated temperature exposure tests may also be found in the same section. This section describes the test specimen loading distribution for each capsule exposure test; it also presents the vacuum furnace time-temperature profile for the long-term exposure tests. The results of tests performed on test specimens before and after exposure are also presented here.

#### a. ALKALI-METAL EXPOSURE TEST PLAN

Five elevated temperature exposure tests of ceramics and ceramic-to-metal seal systems were planned.

- Test 1 - 500-hour, 1600° F tests in potassium and vacuum, of new ceramic-to-metal sealing systems.
- Test 2 - 500-hour, 1600° F tests in potassium and vacuum, of yttria ceramic and sections from 4-inch diameter model bore seal capsule No. 1.
- Test 3 - 2000-hour, 1600° F tests in potassium and vacuum, of the two most promising ceramic-to-metal seal systems determined from test 1.
- Test 4 - 500-hour and 2000-hour, 1600° F tests in lithium, of the two best ceramic-to-metal seal systems.
- Test 5 - 2000-hour tests in potassium at a temperature less than 1600° F if all specimens from test 3 failed. (This test was not required.)

(1) Exposure Test No. 1

Test No. 1 consisted of five capsules containing specimens which were to be tested in potassium vapor at 1600° F and four capsules containing specimens to be exposed to vacuum at the same temperature. Two capsules (one with potassium; one for a vacuum control) contained five ceramic modulus-of-rupture bars each of sapphire (100%  $\text{Al}_2\text{O}_3$ ), Lucalox (99.8%  $\text{Al}_2\text{O}_3$ ), yttria (99.99%  $\text{Y}_2\text{O}_3$ ), and Thermalox 998 beryllia (99.8%  $\text{BeO}$ ). Another capsule for potassium exposure contained five Thermalox 998 modulus-of-rupture bars.

Thirty modulus-of-rupture assemblies, twelve vacuum-leak assemblies and twelve tab-peel assemblies (which had been brazed to columbium-1% zirconium metal members with three braze alloys) were divided equally among six capsules. Three capsules contained potassium. Three were for vacuum test. The three brazing alloys used were 68Ti-28V-4Be (with metallized BeO); 60Zr-25V-15Cb (with metallized BeO); and 46Zr-46Ti-4V-4Be. Thermalox 998 beryllia modulus-of-rupture bars from three lots of BeO powder were used in making the assemblies.

Analysis of potassium in a purity test capsule loaded at the same time as the capsules in Test No. 1 indicated an oxygen content of less than 10 ppm. This analysis was made by a referenced source<sup>1</sup> using the mercury amalgamation method.

(2) Exposure Test No. 2

Test No. 2 consisted of three capsules. One capsule contained five BeO modulus-of-rupture bars (sectioned from 4-inch-diameter bore seal No. 1) for 1600° F exposure to potassium vapor. A second capsule contained a section of the seal area from bore seal No. 1. A third capsule, for 1600° F vacuum exposure, contained five specimens from bore seal No. 1, five yttria modulus-of-rupture bars, and five sapphire modulus-of-rupture rods. (Note: It was found in 500-hour test on the NAS3-4162 program (ref. II-1) that mixing high-purity ceramics in one capsule had no affect on the test results.) Analysis of potassium in a purity test capsule loaded at the same time as the test capsules in Test No. 2 showed an oxygen content of 22 ppm using the mercury amalgamation method.

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<sup>1</sup> Mine Safety Appliance Research Corp., Evans City, Pennsylvania

(3) Exposure Test No. 3

This 2000-hour, 1600° F test in potassium and vacuum consisted of five capsules. One capsule contained five modulus-of-rupture assemblies, two tab-peel assemblies, and one vacuum-tight assembly for exposure in potassium vapor; as well as five modulus-of-rupture assemblies for exposure in potassium liquid. All were made with Cb-1Zr metal members brazed to molybdenum-metallized Thermalox 998 BeO bars (two different lots) with alloy 60Zr-25V-15Cb. The second capsule contained five modulus-of-rupture, one vacuum tight and two tab-peel assemblies to be exposed in potassium vapor. The metal member was Cb-1Zr brazed to Thermalox 998 BeO bars (from two different lots) with alloy 56Zr-28V-16Ti. The third capsule for potassium exposure contained five modulus-of-rupture bars each of yttria, Lucalox, and sapphire for exposure in the alkali-metal vapor and three of each for exposure in liquid.

The fourth capsule, for 2000-hour vacuum exposure control test at 1600°F, contained the same distribution as the first capsule in this group. The fifth capsule, for 2000-hour vacuum exposure control test at 1600°F, contained the same distribution as the second capsule in this group.

(4) Exposure Test No. 4

Test No. 4 consisted of three capsules for 500-hour and 2000-hour lithium exposure at 1600° F. The first capsule contained five modulus-of-rupture, one vacuum-tight, and two tab-peel assemblies for alkali-metal vapor exposure and five modulus-of-rupture assemblies for exposure in liquid. All were fabricated using Cb-1Zr metal members brazed to molybdenum-metallized Thermalox 998 BeO modulus-of-rupture bars using alloy 60Zr-25V-15Cb. The specimen distribution in the second capsule was the same as that in the first capsule of this group. The third test capsule contained five modulus-of-rupture, one vacuum-tight and two tab-peel assemblies for test in lithium vapor and five modulus-of-rupture assemblies for test in liquid. Thermalox 998 BeO bars were joined to Cb-1Zr metal members using the 56Zr-28V-16Ti braze alloy with molybdenum metallizing.

Analyses of the lithium in a purity test capsule indicated high nitrogen content (437 ppm)<sup>20</sup>. One

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<sup>20</sup> Analysis performed by Mine Safety Appliance Research Corp., Evans City, Pennsylvania

capsule was removed from test after 486 hours at 1600° F. The test specimens showed definite signs of alkali-metal attack. The other two capsules, containing specimens for 1600° F lithium exposure, were removed from test after 1544 hours at the same time that the 2000-hour potassium test was terminated.

#### b. EXPOSURE TESTING

All Cb-12r capsules containing specimens were heated in the apparatus described in Section II.B.2. One of the two dual furnaces was used for all tests. Capsules from two tests often ran concurrently. The furnace was shut down and opened to install or remove capsules.

The exposure tests were conducted as follows. The furnace was pumped down with a portable roughing pump through a copper tubulation. When the sputter-ion pump was started, the copper tube was pinched off. Pressure in the furnace typically leveled out at approximately  $1 \times 10^{-9}$  torr cold, and dropped steadily at test temperature from the high  $10^{-7}$  torr range at the start of the test to the low  $10^{-9}$  torr range at the end of the test. The temperature-pressure data shown in table II-12 from the second exposure test are typical. During the tests, the bottom thermocouple indicated temperatures ranging between 1635° and 1643° F with an occasional drop to 1625° F. The variation was a daily cycle depending on ambient temperature since input was controlled by a fixed setting on a variable transformer. The thermocouple at the top of the capsule indicated about 1560° F. (The thermocouples were inserted into a dummy capsule mounted at the same radial distance from the heater as the loaded capsules.) The furnace was operated so that the bottom thermocouple matched the readings established during Test No. 1.

The higher-than-1600° F setting was selected because it was believed that the average temperature of the loaded capsules was between the readings of the bottom thermocouple (1640° F) and the top thermocouple (1560° F).

#### c. SPECIMEN CLEANING

After completion of the test, capsules containing the test specimens were opened in the following manner: a 11/16-inch hole was drilled in the top of the capsule using silicone vacuum oil as the lubricant. The capsule was quickly submerged in a beaker containing methyl alcohol. After the reaction stopped, the capsule was rinsed with distilled water. The end of the capsule was then cut off using a carborundum wheel. The specimens were removed and rinsed in de-ionized water, methyl alcohol,

TABLE II-12. Vacuum Furnace Pressure Data on the 500-Hour,  
1600° F Potassium Exposure Test of Bore Seal  
Capsule No. 1 Sections

Time	Pressure (torr)
After weekend Pump-down furnace cold	$1.5 \times 10^{-8}$
Maximum Pressure during heat-up time of 26 hours	$2.0 \times 10^{-6}$
Start of test	$7 \times 10^{-7}$
After 24 hours	$2.6 \times 10^{-8}$
After 50 hours	$1.7 \times 10^{-8}$
After 125 hours	$1.0 \times 10^{-8}$
After 200 hours	$9 \times 10^{-9}$
After 310 hours	$6.5 \times 10^{-9}$
At end of test (at temperature) 557 hours	$5 \times 10^{-9}$
At end of test (at room temperature)	$2 \times 10^{-9}$

and acetone in the listed order. The specimens were dried in vacuum at 200° F before examination and mechanical testing.

The ceramics removed from Test No. 4 developed spontaneous conchoidal fracture patterns on standing after cleaning. During the last test it was found that lithium had diffused some distance into the ceramic. The ceramics had to be soaked for an extended time in low pH acid solution to leach out the lithium; otherwise, upon reaction with air, the ceramic cracked. In this method of cleaning exposed specimens, therefore, a soaking period was required to insure removal of all traces of alkali metal.

d. RESULTS FROM ALKALI-METAL EXPOSURE TESTS

(1) Exposure Test No. 1

Visual observation showed that the yttria ceramic was not significantly affected after 500-hour exposure to potassium at 1600° F. The beryllia ceramics, Lot E (see analysis table B-1, Appendix B) were discolored.

Results of mechanical tests performed on the specimens from Test No. 1 are summarized in tables II-13 and II-14. The 60Zr-25V-15Cb brazing alloy used in joining molybdenum metallized beryllia and columbium-1% zirconium metal member emerged superior to the 68Ti-28V-4Be alloy with metallized beryllia and to the 46Zr-46Ti-4Be-4V alloy.

There was 31 percent degradation in the flexural strength in specimens brazed with the 60Zr-25V-15Cb brazing alloy after exposure to potassium, but no change in tab peel strength or vacuum integrity. However, when compared to the specimens which had been exposed to vacuum environment at the same temperature and time period, the degradation in strength was 13 percent.

Specimens brazed with 68Ti-28V-4Be brazing alloy degraded 42 percent in flexural strength from the as-brazed condition. Tab peel strength was essentially unchanged, although the absolute values were low. There was no change in vacuum integrity or in flexural strength of the vacuum-exposed specimens.

The specimens brazed with 46Zr-46Ti-4V-4Be alloy degraded in all aspects except for tab peel strength. The as-brazed values were also low.

Results obtained on the ceramics alone (table II-14) show that strength of yttria was unaffected by exposure to potassium at 1600° F for 500 hours. The beryllia modulus bars, lot E, (this lot contained 150 ppm Si) suffered a 20 percent loss in flexural strength after exposure to potassium when compared to the as-received condition.

TABLE II-13. Effect of 500-Hour, 1600°F Potassium Exposure on Room Temperature Flexural and Tab Peel Strength of Beryllia to Cb-1Zr Brazed Systems

Ceramic Body	Metal Member	Braze Alloy (weight percent)	Braze Temperature (°F)	Braze Hold Time (min)	Key	Room Temperature Flexural Strength (psi) <sup>(a)</sup>			Tab Peel Strength <sup>(b)</sup> (pounds/inch)			Vacuum Leak Test (fraction vacuum tight) <sup>(c)</sup>	
						As Brazed	Vacuum Exposed 500 Hrs. 1600°F	Potassium Exposed 500 Hrs. 1600°F	As Brazed	Vacuum Exposed 500 Hrs. 1600°F	Potassium Exposed 500 Hrs. 1600°F	Vacuum Exposed 500 Hrs. 1600°F	Potassium Exposed 500 Hrs. 1600°F
Thermalox 998 (99.8% BeO)	Cb-1Zr	68Ti-28V-4Be (Molybdenum wetting layer)	2372	10	x s n	18 800 1 240 4	18 660 1 660 5	10 950 2 540 4	6.5 ±0.5 2	7.5 ±1.5 2	7.0 ±2.0 2	2/2 -- 2	2/2 -- 2
Thermalox 998 (99.8% BeO)	Cb-1Zr	46Zr-46Ti-4Be-4V	1832	10	x s n	17 800 1 865 5	13 380 420 4	11 530 970 4	6.5 ±0.5 2	10.5 ±5.5 2	6.5 ±0.5 2	1/2 -- 2	2/4 -- 2
Thermalox 998 (99.8% BeO)	Cb-1Zr	60Zr-25V-15Cb (Molybdenum wetting layer)	2436	10	x s n	22 170 2 850 5	17 560 3 530 4	15 250 995 4	52.5 ±2.5 2	85.0 ±5.0 2	50.0 ±20.0 2	4/4 -- 4	4/4 -- 4
Thermalox 998 (99.8% BeO)	Cb-1Zr	56Zr-28V-16Ti	2372	5	x s n	20 100 1 606 16	16 300 1 250 5	13 200 <sup>(d)</sup> 4 100 5	36.0 4.0 6	30.0 -- 2	50.0 -- 2	3/3 -- 3	4/4 -- 4
<p><b>Key</b>    x - arithmetic mean                  s - standard deviation                  n - number of specimens tested</p> <p><b>Notes:</b></p> <p>(a) Strength determinations were made by four point loading on 0.1 inch x 0.1 inch x 1 inch modulus-of-rupture specimens. Load was applied at the rate of 0.1 inch per minute.</p> <p>(b) Tap peel test on 0.1-inch wide by 1.0-inch long strip pulled perpendicularly at 1.0-inch per minute.</p> <p>(c) Vacuum tight indicates helium leak rate of <math>&lt;10^{-9}</math> torr liters/sec.</p> <p>(d) One specimen broke at 7 000 psi in the ceramic/braze interface. The average is 14 750 psi without this specimen.</p>													



TABLE II-14. Effect of 500 Hours Exposure to Potassium Vapor at 1600°F on Room Temperature Flexural Strength of Selected Ceramics

Ceramic Body	Key	Room Temperature Flexural Strength <sup>(a)</sup> Unexposed Control Specimens (psi)	Room Temperature Flexural Strength <sup>(a)</sup> Control Specimens After 1600°F, 500 hrs, Vacuum only (psi)	Room Temperature Flexural Strength <sup>(a)</sup> Exposed Specimens After 1600°F, 500 hrs in Potassium Vapor (psi)
Yttria <sup>(b)</sup> (99.99% Y <sub>2</sub> O <sub>3</sub> )	$\bar{x}$ s n	16 825 4 260 4	16 600 2 890 5	18 600 3 440 4
Thermalox 998 (99.8% BeO) (Lot E)	$\bar{x}$ s n	19 820 1 420 5	21 100 1 410 5	15 850 224 4
<p>Key <math>\bar{x}</math> - arithmetic average s - standard deviation n - number of specimens tested</p> <p>(a) Strength determinations were made by four point loading on 0.1 inch x 0.1 inch x 1 inch modulus-of-rupture specimens. Load was applied at the rate of 0.1 inch per minute.</p> <p>(b) For analysis see Appendix B.</p>				

(2) Exposure Test No. 2

The results on the 500-hour, 1600° F potassium exposure, and post exposure evaluation of sections from a 4-inch-diameter model bore seal are all reported in Section II.C.8.

The Lucalox, sapphire and yttria modulus-of-rupture bars were removed from exposure capsules at the same time as the sections from the model bore seal. Test results are presented in table II-15.

No effect of potassium exposure on Lucalox alumina was noted. Sapphire showed no degradation in strength after 557-hour exposure to potassium at 1600° F. Some strength values for sapphire appear higher after

TABLE II-15. Room Temperature Flexural Strength of Ceramic Modulus-of-Rupture Bars Exposed to Vacuum or Potassium Vapor at 1600°F for 557 Hours

Specimen Description	n	$\bar{x}$	s
Lucalox, in vacuum	5	32,700	1,400
Lucalox, in K vapor	4	32,100	2,000
Lucalox, clean fired only(a)	5	34,000	5,000
Lucalox, in vacuum 500 hours(a)	2	33,000	3,500(b)
Lucalox, in K vapor 500 hours(a)	4	29,800	1,200
Sapphire, in vacuum, capsule	5	76,800	8,100
Sapphire, in K vapor, capsule	3	83,400	2,600
Sapphire, clean fired only(a)	5	63,100	21,000
Sapphire, in vacuum 500 hours(a)	2	78,400	4,300(b)
Sapphire, in K vapor 500 hours(a)	5	76,100	11,000
Yttria, in vacuum	2	16,900	2,100(b)
Yttria, in K vapor	1	10,800	--
Yttria, clean fired only(c)	4	16,800	4,300
Yttria, in vacuum 500 hours(c)	4	16,600	2,900
Yttria, in K vapor 500 hours(c)	4	18,600	3,400

LEGEND: n = number of specimens  
 $\bar{x}$  = arithmetic mean modulus of rupture  
s = Standard deviation

(a) Data from Bore Seal Topical Report NASA-CR-54093 for comparison.  
(b) Deviation of each specimen from the arithmetic mean.  
(c) From table II-14.

potassium exposure, but this is not significant because of the large scatter in data. This scatter is due to random specimen orientation which occurs during testing. Sapphire displays anisotropy in mechanical and physical properties. A number of yttria bars broke spontaneously after cleaning in the manner described earlier. One bar tested had a flexural strength value of 10,800 psi. The degradation in this case was probably caused by the post exposure penetration of reaction products formed during the alkali-metal neutralization and cleaning operation on the slightly porous ceramic.

### (3) Exposure Test No. 3

Room temperature flexural strength was determined on brazed ceramic-to-metal assemblies after exposure to potassium and vacuum for 2000 hours at 1600° F. After each brazed modulus-of-rupture assembly was tested, one section of ceramic from each assembly was tested. The latter test provided data on the strength of the ceramic member after it had been subjected to brazing conditions and alkali-metal exposure.

These data as well as tab peel strength and vacuum integrity are presented in table II-16. Tab peel strength was determined on brazed tab peel assemblies and vacuum integrity on vacuum tight assemblies.

The vacuum-tight assemblies remained vacuum tight after 2000-hour exposure at 1600° F in vacuum or potassium vapor environments. There was some degradation of flexural strength of modulus-of-rupture assemblies which had been brazed with either the 60Zr-25V-15Cb alloy or the 56Zr-28V-16Ti alloy and exposed to potassium vapor. However, all except one of the ten assemblies tested broke in the ceramic. On the other hand, definite degradation was found in the potassium-liquid exposed modulus-of-rupture assemblies brazed with the 60Zr-25V-15Cb alloy. In this case the fractures in all specimens except one occurred in the brazed joint.

The brazement surface exposed after fracture was discolored. Two assemblies retained full strength. No specimens made with the 56Zr-28V-16Ti brazing alloy were exposed to liquid potassium. An apparent degradation occurred in strength of the vacuum exposed assemblies. All fractures occurred in the ceramic. All tab peel strength values for both

alloy systems were high compared to previous test values.

The degradation in strength of brazed modulus-of-rupture assemblies over the ceramic alone was significant in the test results. This may be seen by comparing results in the ceramic column in table II-16 to the strength shown in the assembly column. A surviving ceramic bar from a brazed modulus-of-rupture assembly was tested after the modulus-of-rupture assembly was tested. The same four-point loading technique was used in each case. The assembly strength varied from 70 to 83 percent of the strength in the ceramic alone, when considering the brazed assemblies in which the fracture occurred in the ceramic. The modulus-of-rupture assembly strength of specimens exposed to vacuum as well as to potassium exhibited this degradation in strength as compared to the ceramic strength. Since nearly every tested assembly broke in the ceramic near the brazed joint, it appeared that the ceramic was weakened after the brazing process by diffusion of impurities into the ceramic or by stresses induced in the ceramic. It was noted in the potassium exposed modulus-of-rupture assemblies, that there was a greater tendency to break in the ceramic near the brazed joint (even under the fillet) than in the case of modulus-of-rupture assemblies in the as-brazed condition.

#### (4) Exposure Test No. 4

This test in lithium was more severe than originally anticipated for a static test since the specimens were subjected to a refluxing action during the exposure test. One modulus-of-rupture assembly survived lithium exposure for 1544 hours at 1600° F and retained measurable strength (see table II-16). The Thermalox 998 beryllia ceramics maintained near full strength even though the brazements disintegrated and lithium had penetrated the ceramic to a considerable depth.

#### e. RESULTS AND ANALYSIS OF ALKALI METAL COMPATIBILITY TESTS WITH TWO CERAMIC-TO-METAL SEAL SYSTEMS

Figure II-38 shows graphically a summary of the results on the effect of potassium and elevated temperature vacuum exposure on the flexural strength of 99.8% beryllia ceramic modulus-of-rupture assemblies brazed with the two best alloys, 60Zr-25V-15Cb (beryllia metallized with Mo) and 56Zr-28V-16Ti. Flexural strength is plotted at

several exposure times for different exposure conditions for various lots of beryllia, and modulus-of-rupture assemblies brazed with two brazing alloys. The length of lines in the figure represent the standard deviation envelope about the average flexural strength. Interpretation of the data may be made with the aid of table II-17.

As-brazed modulus-of-rupture assemblies (consisting of two ceramic modulus-of-rupture bars butt-brazed, with a Cb-12r metal member between the bars) usually broke about 0.1 to 0.2 inch from the brazement when the joint was stronger than the ceramic. Often, two or three breaks resulted. Reference strength of the ceramic was obtained by testing cleaned, unbrazed modulus-of-rupture bars. While testing specimens for exposure test No. 3, it was noted that some breaks occurred very near the joint, though still in the ceramic. Therefore, some of the nearly full length ceramics remaining from the broken assemblies were then tested. The values appeared significantly different (usually higher than the strength of the assemblies) so ceramics remaining from all tested assemblies were then tested. The resulting data were extremely significant.

Four lots of beryllia ceramic (figure II-38 and table B-1, Appendix B) having different strengths were used in the exposure tests. The higher strength of lot AA resulted from the slightly smaller cross section of these bars sectioned from the 4-inch diameter ceramic bore seal tube. This ceramic was in the as-brazed condition. In table II-17, comparisons are made according to percentage change from the as-received strength values.

By a study of the data plotted in figure II-38 a number of conclusions may be drawn from the interrelationships of ceramic lots, brazing alloy temperatures, and exposure conditions.

- 1) The room temperature strength of the brazed BeO ceramic did not appear to be affected by 1600° F vacuum exposure for 500 hours or 2000 hours. Ceramics brazed with alloy 60Zr-25V-15Cb (brazing temperature 2436° F) were affected less by 1600° F vacuum exposure than ceramics brazed with 56Zr-28V-16Ti (brazing temperature 2372° F).
- 2) The effect of alkali metal vapors on the room temperature flexural strength of the BeO ceramic is slight after 500- and 2000-hour exposure to potassium or 500- and 1544-hour exposure to lithium. When the strength of alkali-metal vapor exposed ceramic is compared to vacuum exposed ceramic rather than to the as-received ceramic, the effect of alkali metal is even

TABLE II-16. Effect of 1600°F Exposure to Potassium, Lithium, and Vacuum on the Room Temperature Flexural Strength, Tab Peel Strength, and Vacuum Integrity of 99.8% Beryllia to Columbium-1% Zirconium Brazed Systems

Ceramic Body <sup>(a)</sup> Lot B	Metal Member	Braze Alloy (weight percent)	Brazing <sup>(b)</sup> Temperature (°F)	Test Environment at 1600°F	Key	Room Temperature Flexural Strength <sup>(c)</sup> After Exposure Noted in the Test Environment Column (psi)		Tab Peel Strength <sup>(e)</sup> After Exposure Noted in the Test Environment Column (pounds/inch)	Vacuum Leak Test <sup>(f)</sup> After Exposure Noted in the Test Environment Column (fraction vacuum tight)
						Brazed Modulus of Rupture Assembly	Ceramic Only <sup>(d)</sup>		
Thermalox 998 Beryllia 99.8% BeO	Cb-1 Zr	60 Zr-25V-15Cb	2462	Potassium Vapor 2000 hours	$\bar{x}$ s n	21 400 2 100 5	25 500 1 200 5	90 - 2	2/2
Thermalox 998 Beryllia 99.8% BeO	Cb-1 Zr	60 Zr-25V-15Cb	2462	Potassium Liquid 2000 hours	$\bar{x}$ s n	(g) 5	22 600 1 000 5	None Tested	None Tested
Thermalox 998 Beryllia 99.8% BeO	Cb-1 Zr	56 Zr-28V-16Ti	2372	Potassium Vapor 2000 hours	$\bar{x}$ s n	13 200 <sup>(h)</sup> 4 100 5	19 900 1 400 5	50 ±20 2	4/4
Thermalox 998 Beryllia 99.8% BeO	Cb-1 Zr	60 Zr-25V-15Cb	2462	Vacuum 2000 hours	$\bar{x}$ s n	18 200 3 200 5	25 800 1 400 5	70 ±20 2	2/2
Thermalox 998 Beryllia 99.8% BeO	Cb-1 Zr	56 Zr-28V-16Ti	2372	Vacuum 2000 hours	$\bar{x}$ s n	16 300 1 250 5	22 700 2 100 5	30 ±10 2	3/3
Thermalox 998 Beryllia 99.8% BeO	Cb-1 Zr	60 Zr-25V-15Cb	2462	Lithium Vapor 487 hours	$\bar{x}$ s n	(k)	19 600 3 000 5	(j)	0/2
Thermalox 998 Beryllia 99.8% BeO	Cb-1 Zr	60 Zr-25V-15Cb	2462	Lithium Liquid 487 hours	$\bar{x}$ s n	(k)	21 000 2 700 5	(k)	None Tested
Thermalox 998 Beryllia 99.8% BeO	Cb-1 Zr	60 Zr-25V-15Cb	2462	Lithium Vapor 1544 hours	$\bar{x}$ s n	2 200 1 <sup>(m)</sup>	21 000 100 5	(j)	0/2 <sup>(l)</sup>
Thermalox 998 Beryllia 99.8% BeO	Cb-1 Zr	56 Zr-28V-16Ti	2372	Lithium Vapor 1544 hours	$\bar{x}$ s n	(k)	20 950 1 600 5	(k)	0/2
Thermalox 998 Beryllia 99.8% BeO	Cb-1 Zr	56 Zr-28V-16Ti	2372	Lithium Liquid 1544 hours	$\bar{x}$ s n	(k)	19 400 4 500 5	(k)	None Tested

TABLE II-16. Continued

Key:  $\bar{x}$  - arithmetic mean  
 s - standard deviation  
 n - number of specimens tested

Notes:

- (a) All beryllia ceramics obtained from the Prush Beryllium Company. Chemistry and density of several lots were reported in Appendix B.
- (b) Brazing was conducted by heating slowly in a vacuum furnace to 2102°F for the 56Zr-28V-16Ti alloy and holding for 10 minutes; then raising to 2372°F and holding for 5 minutes. For the 60Zr-25V-15Cb alloy, the temperature was raised to 2202°F, held for 10 minutes; then raised to 2462°F and held for 5 minutes. The pressure during heat-up and brazing did not exceed  $1 \times 10^{-6}$  torr. All ceramics brazed with 60Zr-25V-15Cb alloy were metallized with molybdenum before brazing.
- (c) Strength determinations were made by four point loading on two 0.1 inch x 0.1 inch x 1 inch modulus-of-rupture specimens brazed to Cb-1 Zr metal. The load was applied at the rate of 0.1 inch per minute. All assemblies broke in the ceramic near the joint unless otherwise noted. The strength of as-brazed assemblies brazed with 60Zr-25V-15Cb ranged from 21 100 to 23 300 psi among several lots of beryllia. For 56Zr-28V-16Ti, the range was 18 700 to 20 800 psi.
- (d) After breaking the brazed specimen, a remaining section of the ceramic was tested by the same method as described in (c). As-received strength of the ceramic ranged from 19 800 to 24 700 psi.
- (e) Tab peel tests were made on 0.1 inch wide by 1.0 inch long brazed strip of Cb-1 Zr pulled perpendicularly from the ceramic at 1.0 inch per minute. Tab peel strength of as-brazed specimens ranged from 50 to 65 pounds per inch for the 60Zr-25V-15Cb alloy and 30 to 47 lb/in. for 56Zr-28V-16Ti alloy.
- (f) VT - vacuum tight indicates a helium leak rate of less than  $10^{-9}$  torr-liter per second.
- (g) Too varied to calculate s. The actual strength values were: 2 500, 2 100, 13 400, 24 300, and 22 600. The assembly showing 4100 psi result proved to be incompletely brazed. All specimens broke in the braze except the 13 400 specimen which broke at the ceramic-braze interface.
- (h) One specimen broke at 7000 psi at the ceramic-braze interface, others in the ceramic near the braze joint.
- (j) One specimen was intact. The metal pulled off with no measurable force.
- (k) Specimen was not suitable for a test.
- (l) Micro leak. Specimen was intact.
- (m) One specimen tested, others not suitable for a test.

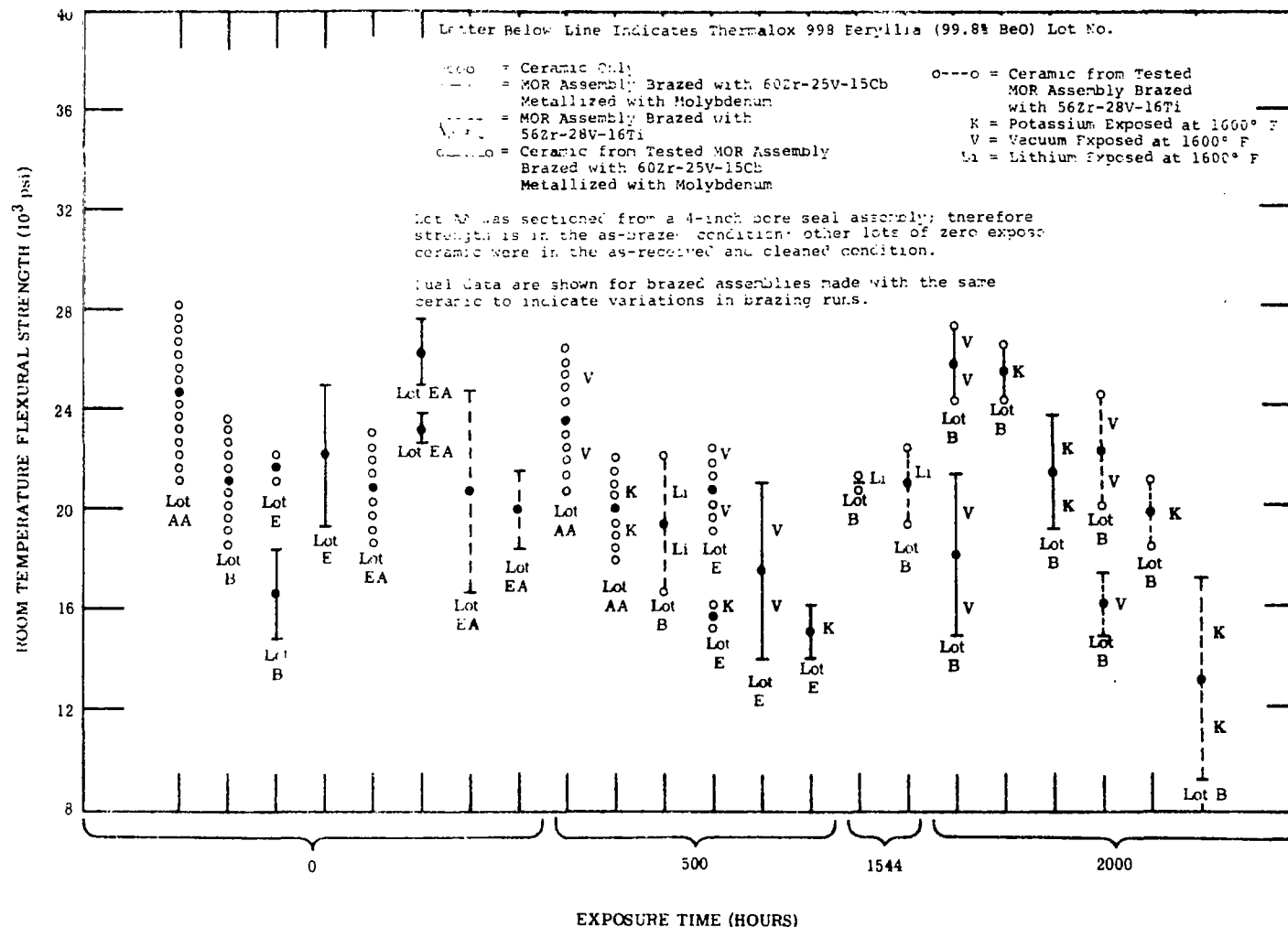


FIGURE 11-38. Graphic Summary of Room Temperature Flexural Strength of Thermalox 998 Beryllia Bars and Brazed Modulus-of-Rupture Assemblies as Associated with Various Exposure Conditions



TABLE II-17. Summary of Effects of 1600°F Vacuum and Potassium Exposure on Room Temperature Flexural Strength of Modulus-of-Rupture Bars and Room Temperature Strength of Modulus-of-Rupture Assemblies

Beryllia Lot Number and Brazing Alloy (a)		Change in Flexural Strength After 500 Hours Exposure as Noted (percent)	Change in Flexural Strength After 2000 Hours Exposure as Noted (percent)
Lot No.	Brazing Alloy		
Effect of vacuum exposure on ceramics compared to clean-fired material (b) (c)			
BeO-AA		-4	-
BeO-B	60Zr-25V-15Cb(Mo)	-	+22
BeO-B	56Zr-28V-16Ti	-	+7
BeO-E		-4	-
Effect of vacuum exposure on ceramics in MOR assemblies compared to clean-fired material (c)			
BeO-B	60Zr-25V-15Cb(Mo)	-	-14
BeO-B	56Zr-28V-16Ti	-	-24
BeO-E	60Zr-25V-15Cb(Mo)	-21	-
Effect of potassium exposure on ceramics compared to clean-fired material (b) (c)			
BeO-AA		-19	-
BeO-B	60Zr-25V-15Cb(Mo)	-	+21
BeO-B	56Zr-28V-16Ti	-	-6
BeO-E		-	-
Effect of potassium exposure on ceramics in MOR assemblies compared to clean-fired material (b) (c)			
BeO-B	60Zr-25V-15Cb(Mo)	-	+1
BeO-B	56Zr-28V-16Ti	-	-32
BeO-E	60Zr-25V-15Cb(Mo)	-32	-
Effect of potassium exposure on ceramics minus vacuum exposed effect (b)			
BeO-AA		-15	-
BeO-B	60Zr-25V-15Cb(Mo)	-	-1
BeO-B	56Zr-28V-16Ti	-	-13
BeO-E		-24	-
Effect of potassium exposure on ceramics in MOR assemblies minus vacuum exposed effect (b)			
BeO-B	60Zr-25V-15Cb(Mo)	-	+15
BeO-B	56Zr-28V-16Ti	-	-12
BeO-E	60Zr-25V-15Cb(Mo)	-11	-

TABLE II-17. Continued

Beryllia Lot Number and Brazing Alloy (a)		Exposure	Change in Flexural Strength After 2000 Hours Exposure Compared with Clean- Fired Material <sup>(c)</sup> (percent)
Lot No.	Brazing Alloy		
BeO-B	60Zr-25V-15Cb(Mo)	Vacuum	-36
BeO-B	60Zr-25V-15Cb(Mo)	Potassium	-20
BeO-B	56Zr-28V-16Ti	Vacuum	-31
BeO-B	56Zr-28V-16Ti	Potassium	-31
BeO-E	60Zr-25V-15Cb(Mo)	Vacuum	-17
BeO-E	60Zr-25V-15Cb(Mo)	Potassium	- 4
BeO-E	60Zr-25V-15Cb(Mo)	As Brazed, 2436°F for 5 min.	~20
BeO-E	60Zr-25V-15Cb(Mo)	As Brazed, 2516°F for 5 min.	-24
BeO-EA	60Zr-25V-15Cb(Mo)	As Brazed, 2516°F for 5 min.	+26
BeO-EA	60Zr-25V-15Cb(Mo)	As Brazed, 2436°F for 5 min.	+11
BeO-EA	56Zr-28V-16Ti	As Brazed, 2370°F for 5 min.	~20
BeO-EA	56Zr-28V-16Ti	As Brazed, 2370°F for 5 min.	- 4
(a) See Appendix B for ceramic compositions. (b) If no brazing alloy is listed, data are for bare ceramics, if brazing alloy is listed, data are for ceramics remaining after MOR assemblies were broken. (c) Clean-firing was performed in 75%N <sub>2</sub> -25%H <sub>2</sub> (dew point 100°F) at 2597°F for 30 minutes.			

less. However, it may be noted that beryllia lot E, containing 150 ppm Si, showed more significant degradation in alkali metal than two other lots of lower Si beryllia ceramic. This data verified the data reported previously (ref. II-1). The paragraph above defines the thermal-vacuum effects on the various lots of BeO. The degree of differences among the various lots of potassium exposed BeO is less if the thermal-vacuum effect on each lot is subtracted.

- 3) The brazing process appears to have caused reduction of the ceramic-to-metal assembly strength as compared to the ceramic strength in the vacuum exposed specimens. This loss in brazed assembly strength is not usually noted on as-brazed assemblies so may be associated with impurity pickup, or localized stress in the ceramic near the braze joint, or crack (notch sensitivities due to grinding the ceramic members).

- 4) There was degradation in brazed assembly strength in alkali-metal vapor exposed specimens. The degradation by lithium was much more severe than by potassium. However, it may be noted in the exposed specimens that both assembly and ceramic strength, especially the latter, tended to exhibit smaller standard deviations. This may indicate a reduction in the surface flaw concentration with a resulting reduction in stress risers where fracture is initiated.
- 5) Although the strength-reducing effect of the brazing process on the assemblies seemed to be about the same for both brazing alloys, there was a substantial over-all reduction of both ceramic and assembly strengths (figure II-38) associated with the assemblies brazed with 56Zr-28V-16Ti alloy. In all comparisons, without exception, the use of 60Zr-25V-15Cb alloy resulted in stronger assemblies. Reference to table II-16 shows that this superiority also applies to tab peel strength.

Another significant effect seems to be a ceramic strengthening effect associated with the 60Zr-25V-15Cb brazing alloy. This occurred in the case of BeO, lot EA.

- 6) Despite some negative exposure effects, results are very encouraging. The low Si Thermalox 998/60Zr-25V-15Cb/Cb-1Zr combination was selected for fabrication of four-inch diameter model bore seals on the basis of data obtained early in the program. Results of the subsequent tests clearly confirmed this choice.

#### f. ANALYSIS OF THE BeO (60Zr-25V-15Cb) /Cb-1Zr SYSTEM

An analysis of the final selected system was performed. Photomicrographs of cross sections from the 4-inch diameter bore seal No. 1 (trial braze assembly) are shown in figure II-39. Severe erosion of the ceramic and reaction with the Cb-1Zr after brazing is evident. The reaction zone appears to be largely a solid solution.

More detailed examinations were made of brazed specimens (figures II-40 and II-41). Cross sections of both the modulus-of-rupture and vacuum tight assemblies were made. Microstructures of all three exposure conditions are similar. Again, erosion of the BeO and extensive reaction with the Cb-1Zr after brazing is shown. The reaction zone consists mostly of a solid-solution phase with entrapped grains of BeO and some eutectic.

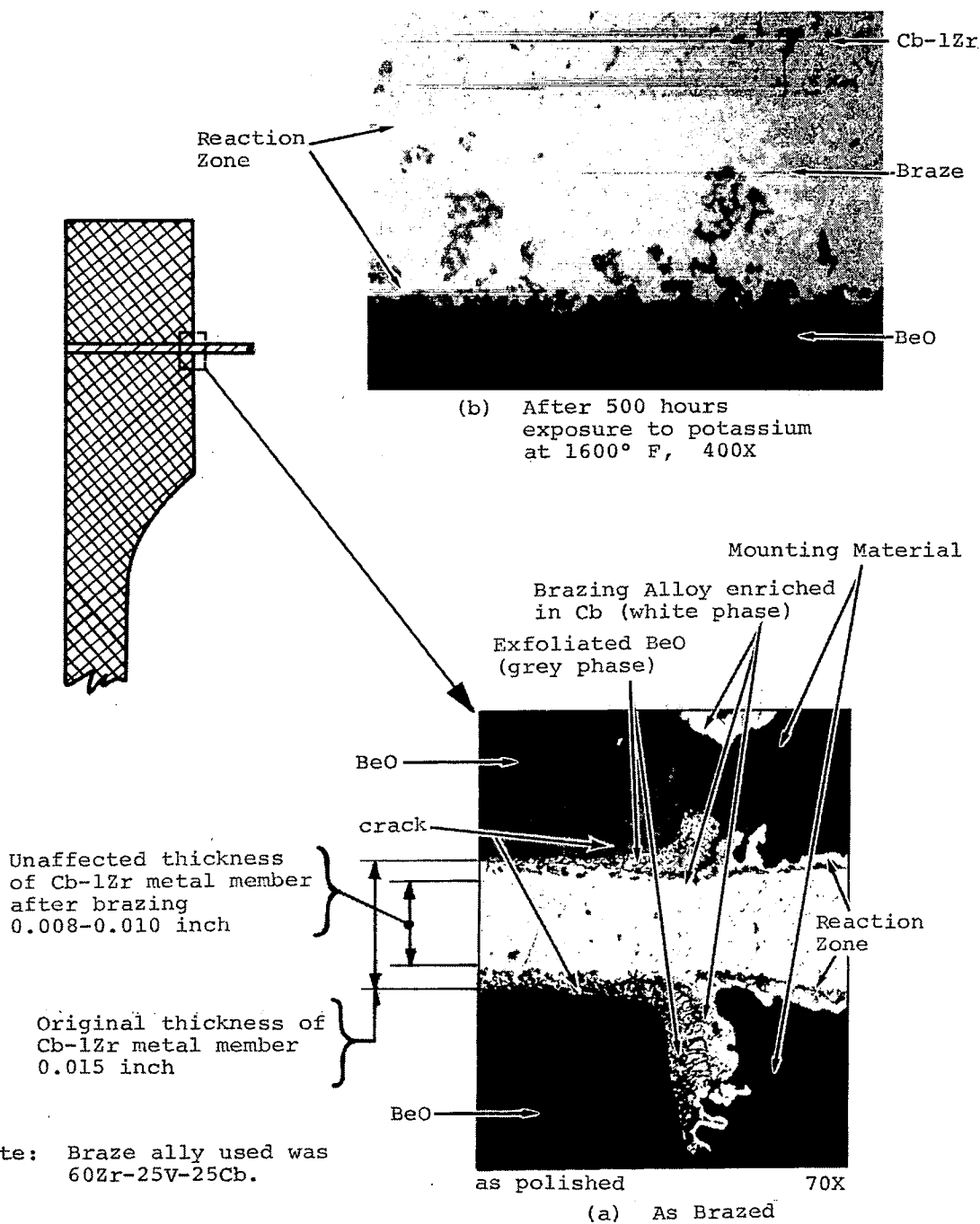
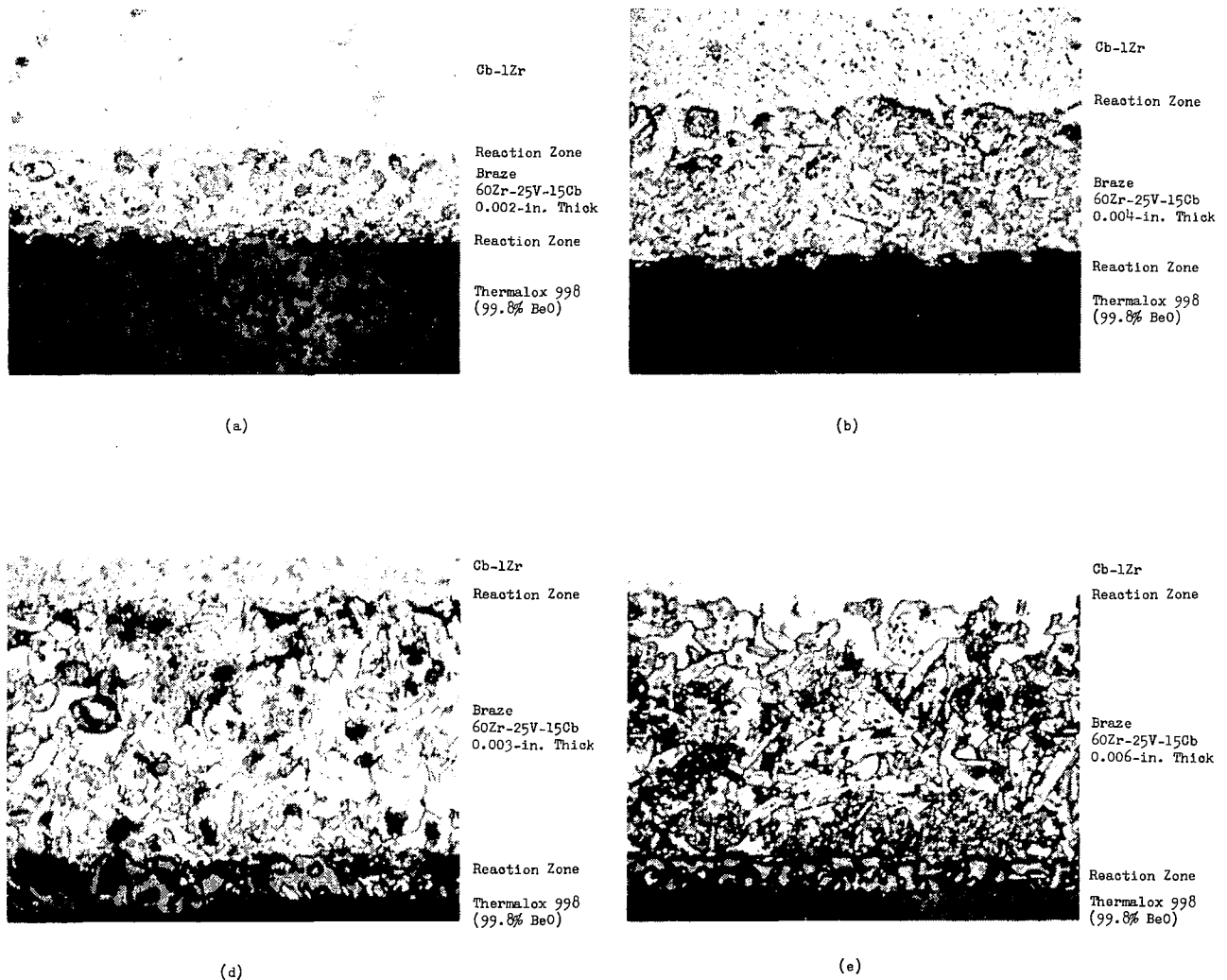


FIGURE II-39. Photomicrographs Showing Cross-Sections of Brazed Joints From 4-Inch Diameter by 4-Inch-High Bore Seal Capsule No. 1 as Brazed and After Exposure to Potassium at 1600° F for 500 Hours. (70X and 400X Before Photo Reductions)



**FIGURE II-40. Photomicrographs Showing Cross-Sections From Sandwich Type Vacuum Leak Tightness Assemblies and Modulus-of-Rupture Bars of Alloy 60Zr-25V-15Cb Between Cb-1Zr and Thermalox 998 (99.8% BeO) After Various Exposure Conditions, 350X**



Cb-12r  
Reaction Zone  
Braze  
60Zr-25V-15Cb  
0.006-in. Thick

Reaction Zone

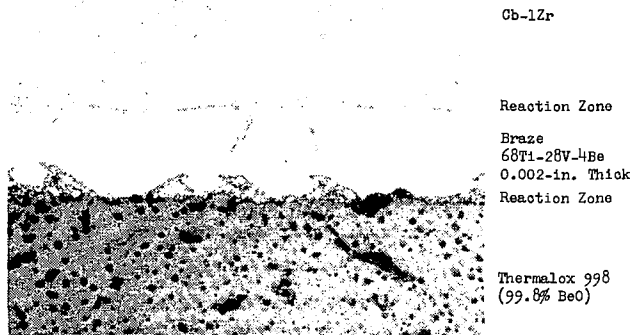
Thermalox 998  
(99.8% BeO)

(o)

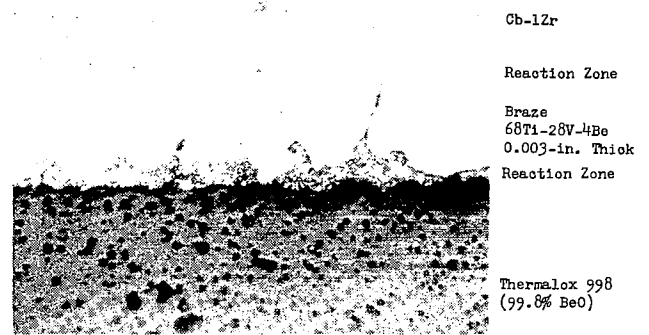
- (a) Vacuum leak tightness assembly joint after 500 hours exposure to vacuum at 1600°F. Vacuum tight after exposure.
- (b) Vacuum leak tightness assembly joint after 500 hours exposure to potassium at 1600°F. Vacuum tight after exposure.
- (c) Modulus-of-rupture assembly joint after 500 hours exposure to vacuum at 1600°F.
- (d) Modulus-of-rupture assembly joint after 500 hours exposure to potassium at 1600°F.
- (e) Modulus-of-rupture assembly joint in the as-brazed condition.

Note: The reaction zone between the braze and BeO is shown in each photomicrograph. These reaction zones consist mostly of solid-solution phase with entrapped grains of BeO and some eutectic but they are not clear at this magnification. In (b) this was partially removed during polishing.

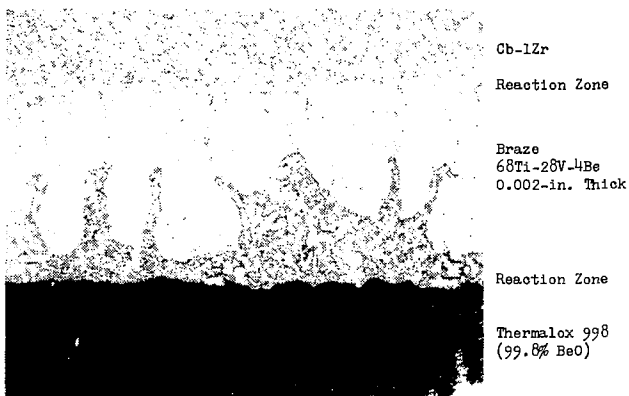
Etchant: 30 ml lactic acid, 30 ml HNO<sub>3</sub>,  
10 ml HF.



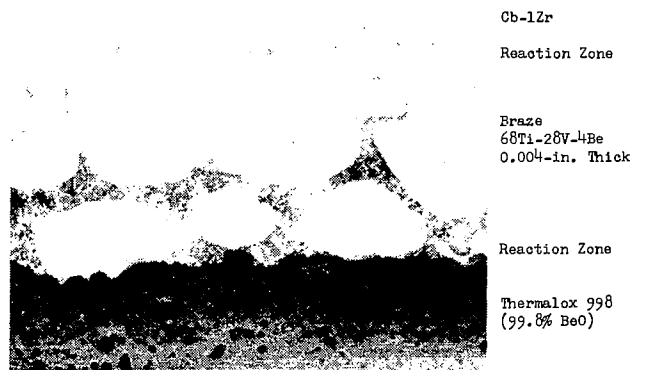
(a)



(b)

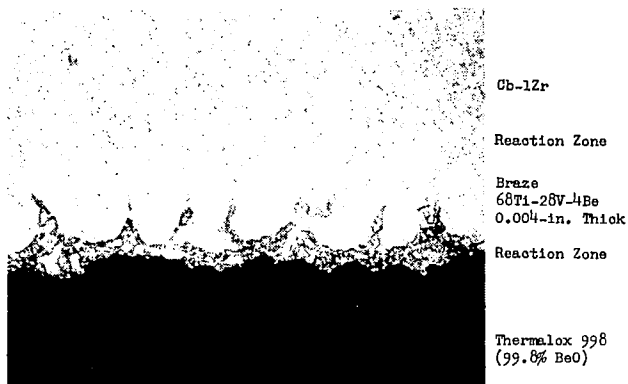


(d)



(e)

**FIGURE II-41. Photomicrographs Showing Cross-Sections From Sandwich Type Vacuum Leak Tightness Assemblies and Modulus-of-Rupture Bars of Alloy 68Ti-28V-4Be Between Cb-12r and Thermalox 998 (99.8% BeO) After Various Exposure Conditions, 350X**



(o)

- (a) Vacuum leak tightness assembly joint after 500 hours exposure to vacuum at 1600°F. Vacuum tight after exposure.
- (b) Vacuum leak tightness assembly joint after 500 hours exposure to potassium at 1600°F. Vacuum tight after exposure
- (c) Modulus-of-rupture assembly joint after 500 hours exposure to vacuum at 1600°F.
- (d) Modulus-of-rupture assembly joint after 500 hours exposure to potassium at 1600°F.
- (e) Modulus-of-rupture assembly joint in the as-brazed condition.

Note: The reaction zone between the braze and BeO is shown in each photomicrograph. These reaction zones consist mostly of solid-solution phase with entrapped grains of BeO and some eutectic but they are not clear at this magnification.

Etchant: 30 ml lactic acid, 30 ml  $\text{HNO}_3$ ,  
10 ml HF.



The reaction zones of the vacuum tight specimens are thinner and appear to have a finer grain structure. The weights used in the brazing fixtures in brazing these specimens resulted in much higher pressure per unit area during brazing. Apparently, some of the brazing alloy had been squeezed out to the sides during the brazing cycle; resulting in more rapid saturation by columbium and faster solidification.

The white phase shown in the as-brazed specimens next to the Cb-1Zr metal member was significantly different from the corresponding faint phase in the exposed specimens. The contrast was even greater at higher magnification. At 800X and higher, a fine particulate phase was observed aligned parallel to the Cb-1Zr surface in this surface phase of the exposed specimens.

No etching method was found in which the beryllia and reaction zone were shown clearly without overetching the Cb-1Zr metal member. The fine grained and quite homogeneous structure of this alloy, compared to the others, is probably a significant reason for its success.

The severe erosion of the ceramic did not appear to be detrimental. In fact, brazing conditions that resulted in erosion produced the strongest seals.

## 7. Properties of Ceramic-to-Metal Seals

Mechanical property tests were conducted on ceramic-to-metal seal assemblies made with two of the most promising seal systems. The following tests complement those already reported and aid the designer in his application of bore seals to space electric power systems. Elevated temperature flexural strength was determined on ceramic-to-metal modulus-of-rupture assemblies. Two-inch diameter beryllia Cb-1Zr model bore seal assemblies were subjected to a combination elevated temperature vacuum leak and thermal shock test. A two-inch diameter model bore seal assembly was also subjected to vibration tests.

### a. ELEVATED TEMPERATURE FLEXURAL STRENGTH TESTS

There was no known information available on the elevated temperature strength of ceramic-to-metal seals. This property has not been determined because the standard ASTM CLM-15 brazed ceramic test specimen is not readily adapted to testing at high temperatures.

The modulus-of-rupture assembly adopted on this program for evaluation of potential ceramic-to-metal seal systems was used for the elevated temperature strength tests. Two Thermalox 998 beryllia modulus-of-rupture bars (0.1-inch by 0.1-inch by 1.1-inch long) were butt-brazed together with a columbium-1% zirconium metal member (0.010-inch thick) between the ceramic bars. Specimens were made with the 60Zr-25V-15Cb active metal brazing alloy. The ends of the ceramic bars were metallized with molybdenum before brazing. Six brazing runs were made to fabricate the modulus-of-rupture assemblies. The standard braze cycle for this alloy was applied as described in Section II.C.4.b(3). The modulus-of-rupture assembly permits additional testing of the ceramic member after the brazed joints had been evaluated.

Elevated temperature modulus-of-rupture tests were conducted in the manner reported in Section II-B.4.a. Specimens were in the as-brazed condition. Test results are shown in table II-18. The data indicate nearly constant strength as a function of temperature to 1600° F. Since all modulus-of-rupture assemblies except one broke in the ceramic, it is concluded that the braze joint remains stronger than the ceramic to 1600° F. The data on the ceramic strength reported here are consistent with the known strength versus temperature behavior of high-purity beryllia referenced in Appendix C.

#### b. VIBRATION TESTS OF TWO-INCH DIAMETER MODEL BORE SEAL ASSEMBLIES

Twenty-four sets of Thermalox 998 (99.8% BeO) ceramics for 2-inch by 2-inch bore seal tubes and back-up rings were received from the vendor. The vendor's analysis is shown in Appendix B (Lot BeO-G).

All ceramics passed dimensional inspection, but excessive surface porosity and roughness were noted. Dye checking revealed many pores in all of the ceramic parts. Cracks were found in 5 tubes and 3 back-up rings. All cracked ceramics were rejected. The 19 accepted tubes were found to be leak tight. The 2-inch diameter vibration test assembly is shown in figure II-13. It consisted of a 2-inch outside diameter by 1.8-inch inside diameter by 2-inch long BeO tube, two washer-like Cb-1Zr flanges and two 2-inch outside diameter by 1.8-inch inside diameter by 0.2-inch long BeO back-up rings (figure II-42).

Ceramics and metals were cleaned and prepared by the standard procedures (see Appendix A). Assemblies were individually brazed, using simple graphite jigs in the

TABLE II-18. Elevated Temperature Flexural Strength of Molybdenum Metallized Beryllia-Columbium-1% Zirconium Assemblies Brazed with 60Zr-25V-15Cb

Test Temperature (°F)	Flexural Strength of Brazed Modulus-of-Rupture Assemblies (a) (b) (psi)	Remarks
1598	20,500	Specimen broke in the ceramic
1408	26,400	Specimen broke in the ceramic
1399	33,500 (c)	Specimen broke in the ceramic
1220	23,200	Specimen broke in the ceramic
1595	18,900	Specimen broke in the ceramic
1395	20,600	Specimen broke at the ceramic/metal interface
1198	42,800 (c)	Specimen broke in the ceramic (c)

(a) All ceramic-metal modulus-of-rupture assemblies consisted of 0.1 inch x 0.1 inch x 1.0 inch Thermalox 998 Beryllia (molybdenum metallized) modulus bars brazed to Columbium-1% zirconium metal with alloy 60Zr-25V-15Cb. Brazing temperature was 2462°F. The brazing cycle was described in the notes for table II-3.

(b) For elevated temperature tests, a clamshell furnace was used in conjunction with an Instron tester. The apparatus was evacuated and back-filled with high-purity argon. The furnace was then heated to 1000°F, outgassed and back-filled. After heating to the test temperature specimens were tested at a strain rate of 0.1-inch per minute.

The average room temperature flexural strength on the same braze system ranged from 21,000 to 23,300 psi among several lots of beryllia ceramic.

(c) The push-rod seized during these tests; thus, breaking force values were less than those indicated by the Instron tester.

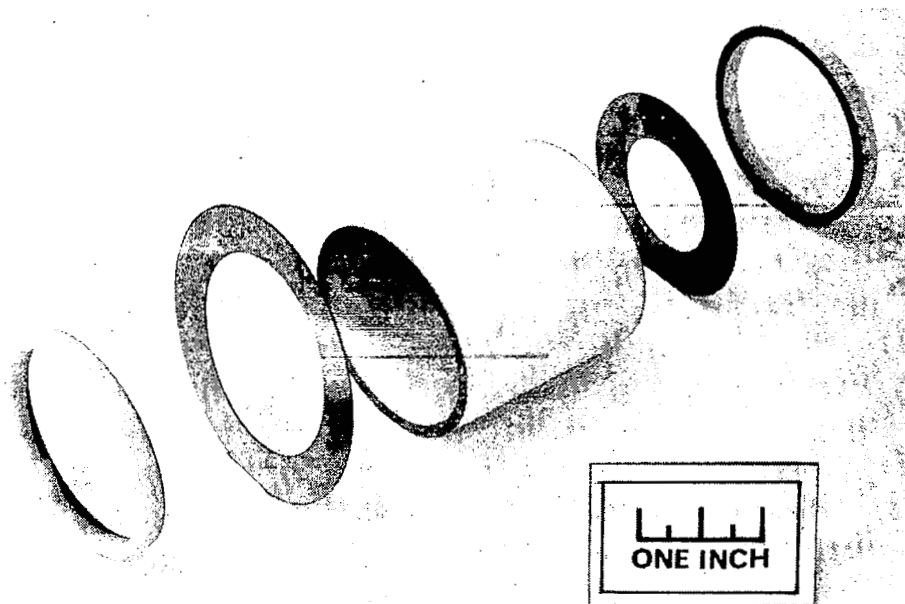


FIGURE II-42. Subassembly of 2-Inch Diameter by 2-Inch Long Thermalox 998 (99.8% BeO) - (Cb-1Zr) Vibration Test Specimen Brazed with 60Zr-25V-15Cb Alloy

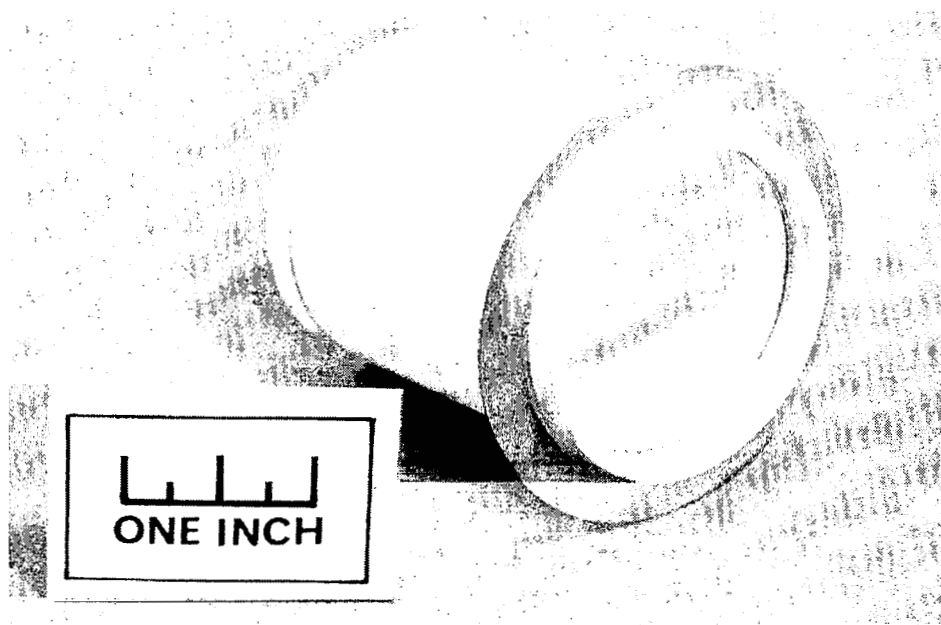


FIGURE II-43. Brazed 2-Inch Diameter by 2-Inch Long Thermalox 998 (99.8% BeO) - (Cb-1Zr) Vibration Test Specimen Brazed with 60Zr-25V-15Cb Alloy

vacuum brazing furnace, by the standard procedure for Alloy 60Zr-25V-15Cb with molybdenum-metallized ceramic. The brazed assembly is shown in figure II-43. One back-up ring used for the second assembly did not seat properly. This assembly was re-brazed at 2500° F using additional brazing material. The assembly was leak tight after re-brazing, but there was excessive filleting. The narrow metal flange between the ceramic tube and back-up ring had cracked radially in three places. The back-up ring on the same end had also cracked in one place.

The end ring on one other assembly did not seat properly after brazing due to improper clearance in the brazing jig. This assembly was made leak tight by re-brazing at 2552° F.

All assemblies were vacuum leak tight before vibration testing. The vibration tests were performed as described in Section II-B.4.b.

Although one of three brazed assemblies remained leak-tight after the vibration test, it was apparent that the assembly design contributed to the failure. The washer-like Cb-1Zr flanges between the ceramic tube and back-up rings were too wide and too stiff. The washer should have been designed with an off-set near the ceramic-to-metal joint as in the 4-inch diameter bore seal test assemblies. This permitted plastic deformation and relieved the joint of excessive stresses.

#### c. ELEVATED TEMPERATURE VACUUM LEAK AND THERMAL SHOCK TEST

It was first planned to conduct elevated temperature leak check tests on small vacuum tight cylinder specimens. Later, a method of combining the test with the thermal cycle tests was devised and carried out. The equipment and test procedure were outlined in Section II-B.4.c. Test specimens were in the form of a model bore seal (figure II-44), with a Cb-1Zr tubulation to form an evacuable assembly. Metal flanges were hydroformed from 0.015-inch thick Cb-1Zr sheet and annealed by the same method as described in Section II-B.1.b. Specimens were individually brazed by the standard schedule (Section II-C.4.b.(3)). The first assembly was brazed with a new lot of 60Zr-25V-15Cb alloy (lot E) obtained to provide enough brazing alloy to complete the program. This assembly was a leaker because of improper melting of the alloy.

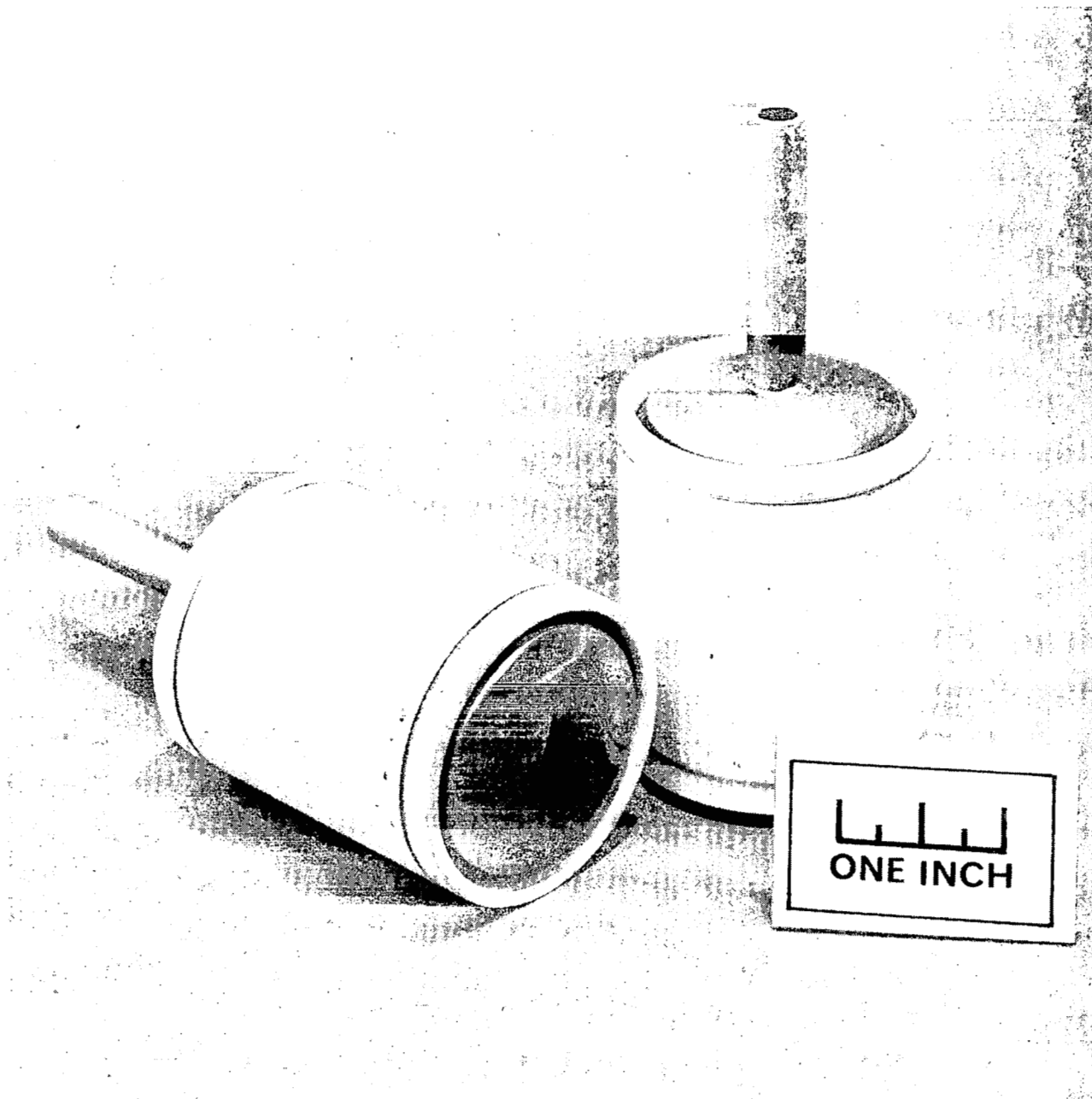


FIGURE II-44. Two-Inch Diameter Thermalox 998 (99.8% BeO) - (Cb-1Zr) Thermal Shock and Vacuum Leak Assemblies Brazed with 60Zr-25V-15Cb Alloy

Difficulty was encountered in fabricating leak tight (leak rate less than  $10^{-9}$  torr-liters per second) assemblies in the 2-inch diameter configuration. Therefore, the change in leak rate was determined before and after thermal shock tests rather than a simple detection of a leak. Brazed assemblies are shown in figure II-44. The test results indicated an increase in the leak rate with an increasing number of thermal cycles. See figure II-45.

8. Fabrication of Four-Inch Diameter by Four-Inch Beryllia-to-Columbium-1% Zirconium Model Bore Seal Capsule

The purpose of this task was to construct a larger model bore seal capsule for endurance testing in potassium and high vacuum while positioned in a high temperature stator cavity. (The stator testing is described in (ref. II-2). The bore seal assembly was constructed using the best sealing system as determined earlier in this program. The Thermalox 998 (99.8% beryllia) portion of the bore seal capsule was 4-inches in diameter by 4-inches long. To provide an intermediate step in scaling up from the 1/2-inch diameter test pieces, bore seals 2 inches in diameter by 2 inches long were to be fabricated and subjected to mechanical and vacuum integrity tests. Because of an unexpectedly long delay in delivery of the 2-inch by 2-inch beryllia ceramics, trial brazes were made with 2-inch diameter by 1/2-inch long beryllia ceramics which were available. The 2-inch by 2-inch specimens were fabricated and tested later in the program (Section II-C.7.). Two leak tight assemblies were made with the 2-inch Thermalox 998 (99.8% beryllia) ceramic and Cb-1Zr metal member using active-metal braze alloy 56Zr-28V-16Ti. Subsequent mechanical, alkali-metal and vacuum integrity tests showed that ceramic-to-metal seals made with Thermalox 998 (99.8% beryllia), (60Zr-25V-15Cb) and Cb-1Zr metal member were superior. The fabrication and potassium loading of 4-inch diameter bore seal capsules using 60Zr-25V-15Cb is described in this section.

a. DESIGN

The model bore seal consisted of a 4-inch outside diameter by 4-inch long 99.8% BeO tube with a 0.1-inch-thick wall, two 4-inch outside diameter by 3.6-inch inside diameter by 0.2-inch long BeO back-up rings, two Cb-1Zr end pieces, and a Cb-1Zr fill tube (figure II-46). The wall of the large beryllia cylinder was 0.2-inch thick at the ends to provide a greater brazing area at the seal. The end piece was made hemispherical to equalize stresses when a differential pressure is imposed on the capsule. The Cb-1Zr tubulation was machined so that a cap could be electron-beam welded on the end after loading with potassium.

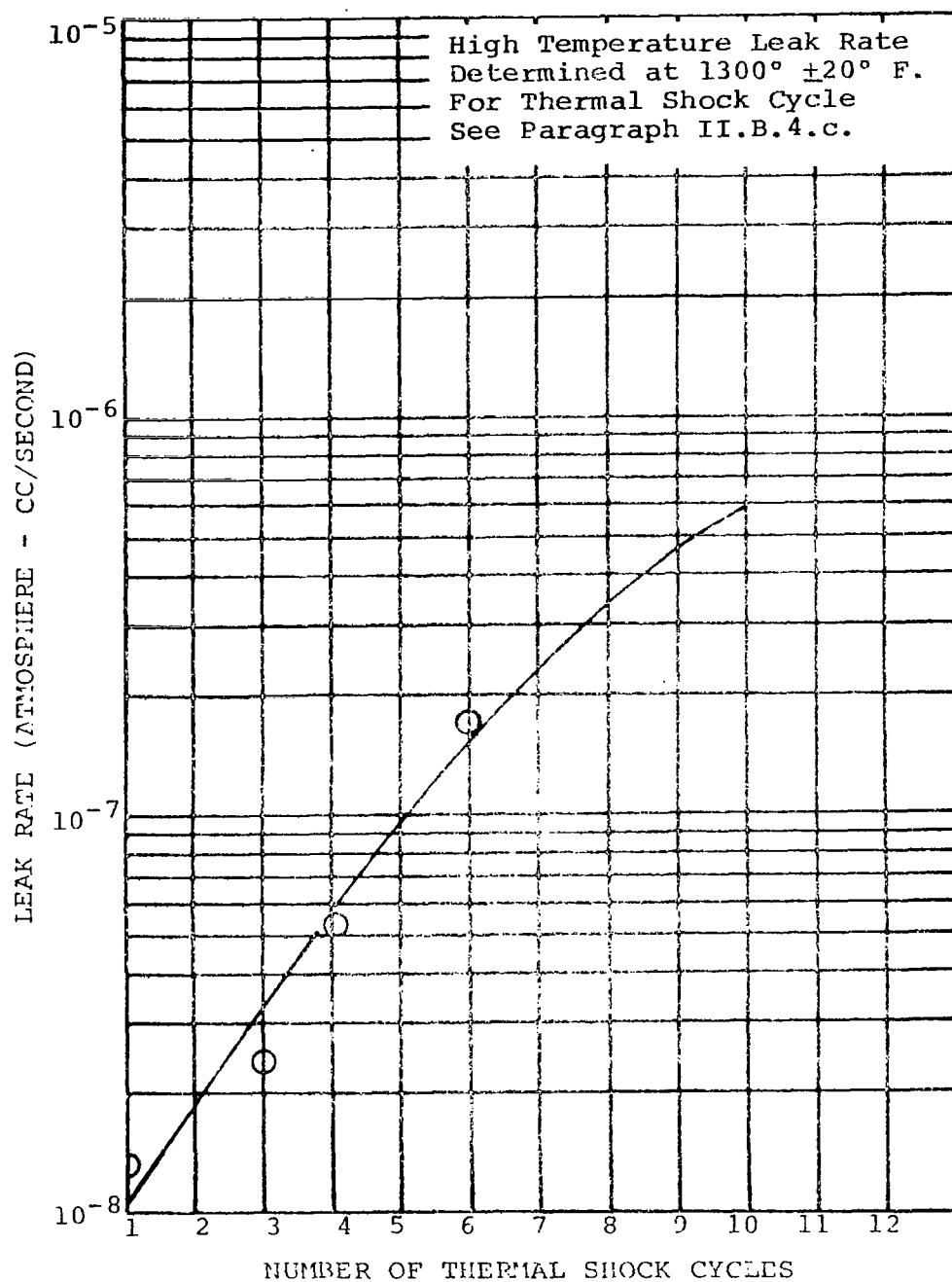


FIGURE II-45. Leak Rate at  $1300^{\circ} \text{ F} \pm 20^{\circ} \text{ F}$  as a Function of Thermal Shock Cycles on Two-Inch Diameter Therma-lox (99.8 BeO) to Cb-1Zr Specimen



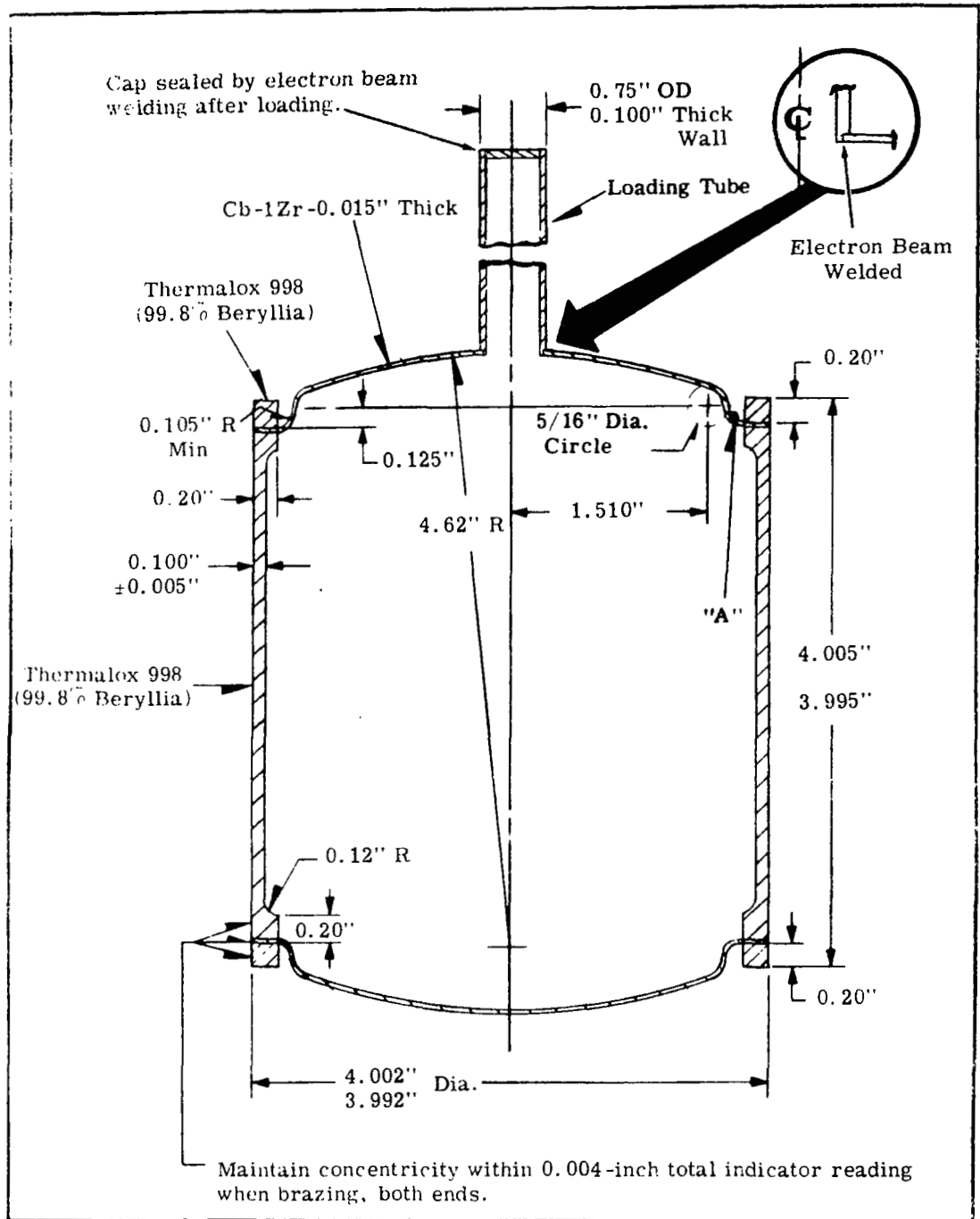


FIGURE II-46. Bore Seal Capsule for Compatibility Test

## b. CERAMIC INSPECTION AND TESTING

Six sets of Thermalox 998 (99.8% beryllia) ceramics (tubes and back-up rings) were ordered for the 4-inch diameter bore seal capsules. Figure II-47 shows a 4-inch beryllia tube after dye checking. The vendor's spectrographic analysis is shown in table II-19. Silicon content of the starting BeO powder was 65 ppm. This was higher than the 50 ppm specified. Other significant points are:

- 1) Iron content of the fired ceramic is lower than that of the pre-fired powder. This is contrary to the vendor's normal experience (ref. II-10).
- 2) Silicon content in the fired beryllia is higher than the starting powder (75 ppm versus 65 ppm) as is usually found (ref. II-10).
- 3) The decrease in sodium content after firing is normal (ref. II-10) because of volatilization during the sintering process.
- 4) No explanation for the change in magnesium content was offered by the supplier (ref. II-10).

The ceramics were inspected for dimensional tolerance and all were acceptable except for excessive surface porosity and roughness. Dye checking revealed many sizable pores (figure II-47). Leak checking disclosed two leaking ceramic tubes. Five of the cylinders were retained and one vacuum leaker was returned for replacement. Subsequently a leak-tight replacement cylinder was received. One rejected cylinder was retained for ceramic-to-metal process development. The ceramics were fired, then cleaned according to procedures reported in Appendix A, MP-1.

## c. PREPARATION OF METAL MEMBERS

End bells (figure II-46 and II-48) were hydroformed from 0.015-inch-thick Cb-1Zr alloy sheet and then cleaned by the procedure reported in Appendix A. The tubulation was welded to the top end bell by electron-beam welding. The end bell was found to warp easily due to the difference between tube wall thickness and thickness of the end bell (see top of figure II-52). A second set was made usable by back-brazing the joint with alloy 60Zr-25V-15Cb during heat treatment. A modified tube design permitting easier welding was devised and was used in subsequent metal members. The modified design was also used in the 2-inch by 2-inch bore seal test assemblies, reported in Section II-C.7.c.

Circled Spots Indicate Pores

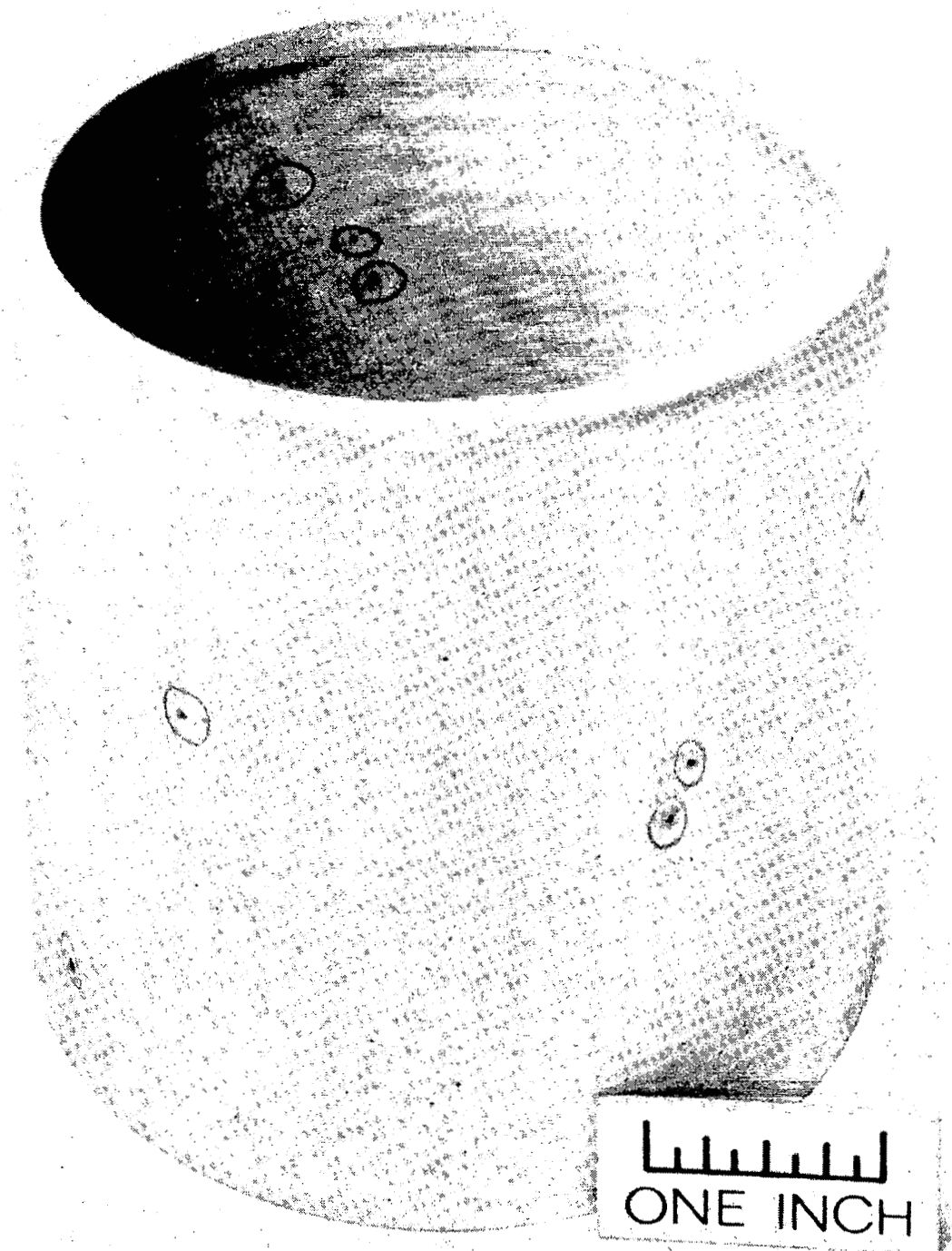


FIGURE II-47. Photograph of Thermalox 998 (99.8% BeO) Tube After Dye Penetrant Check

TABLE II-19. Analyses of Beryllia Powder and Fired Ceramics for the Four-Inch Diameter by Four-Inch High Beryllia Tubes

Constituent	Impurity Content <sup>(a)</sup> Thermalox 998(BeO) Lot AA (ppm)		
	Ready to Press Powder	After Firing In Platinum Crucible (control sample)	Fired Stock (from 4-in. diam tube)
Al	60	70	70
Fe	65	50	45
Ca	65	210	75
Si	65	75	75
Mg	700	850	620
Cr	12	< 3	8
Mn	2	2	2
Ni	10	8	8
B	1	< 1	< 1
Co	< 1	< 1	< 1
Li	2	2	2
Cd	(b)	(b)	(b)
Cu	2	4	< 2
Mo	< 3	< 3	< 3
Na	50	30	30
Ag	< 1	< 1	< 1
Pb	2	< 2	< 2
Ti	3	3	3
Zn	< 20	< 20	< 20
<p>(a) Spectrographic analyses representing the average of three separate analyses from three samples. On all elements except Mg, the variation was <math>\pm 5</math> ppm from the values shown. Analyses by Brush Beryllium Company.</p> <p>(b) Not detected.</p>			

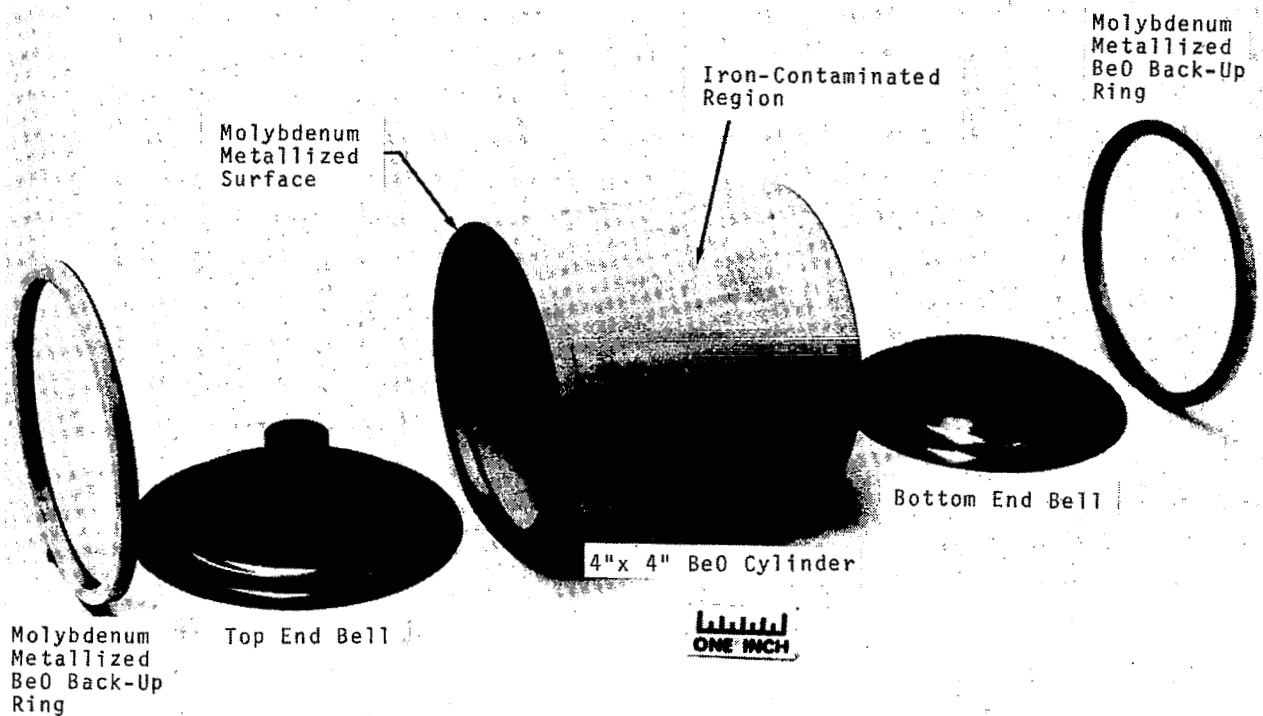


FIGURE II-48. Sub-Assembly of a Model Four-Inch Diameter Thermalox 998 (99.8% BeO) - (Cb-1Zr) Bore Seal

The flanges on the end bells were flattened by the following procedure:

- 1) The flange was mounted in the fixture (figure II-49) with the quality analysis specimen.
- 2) The fixture was then mounted in the 6-inch vacuum brazing furnace (Section II-C.2.c.).
- 3) The parts were heated to 2200° F while keeping the furnace pressure below  $1 \times 10^{-5}$  torr.
- 4) The temperature was held at 2200° F for two hours and cooled to room temperature under vacuum.

The above procedure also annealed the Cb-1Zr end bell. The analysis specimen was a 1-inch square sheet from the same lot of materials as that used in making the end bell. This sheet accompanied the end bell through every handling step during bore seal manufacture so that an estimate of impurity pick-up could be made if desired.

#### d. CERAMIC METALLIZING

The 4-inch beryllia tubes and back-up rings were metallized as described in Appendix A, MP-1. (See also ref. II-11.)

#### e. MODEL BORE SEAL BRAZING

Parts for the 4-inch bore seal No. 1, ready for brazing, are shown in figure II-48. The metallizing shows as the dark surface on the ends of the ceramic. The dark spots on the side of the ceramic are internally stained regions which were attributed to minute iron oxide inclusions. (During sintering the iron reacts with and diffuses into the BeO (ref. II-10).)

- (1) Four-Inch Diameter Bore Seal Capsule No. 1  
(trial braze)

The first bore seal capsule was brazed as follows: alloy 60Zr-25V-15Cb was applied by the powder method described in Appendix A. Preparation of the alloy powder was described in Section II-C.2.b.

Parts were assembled into the brazing fixture (figure II-50) and the brazing run was conducted as previously described in Section II-C.2. Hold time was five minutes at 2426° F. The actual time-temperature/pressure history for the brazing run is shown in figure II-51. The actual run was preceded

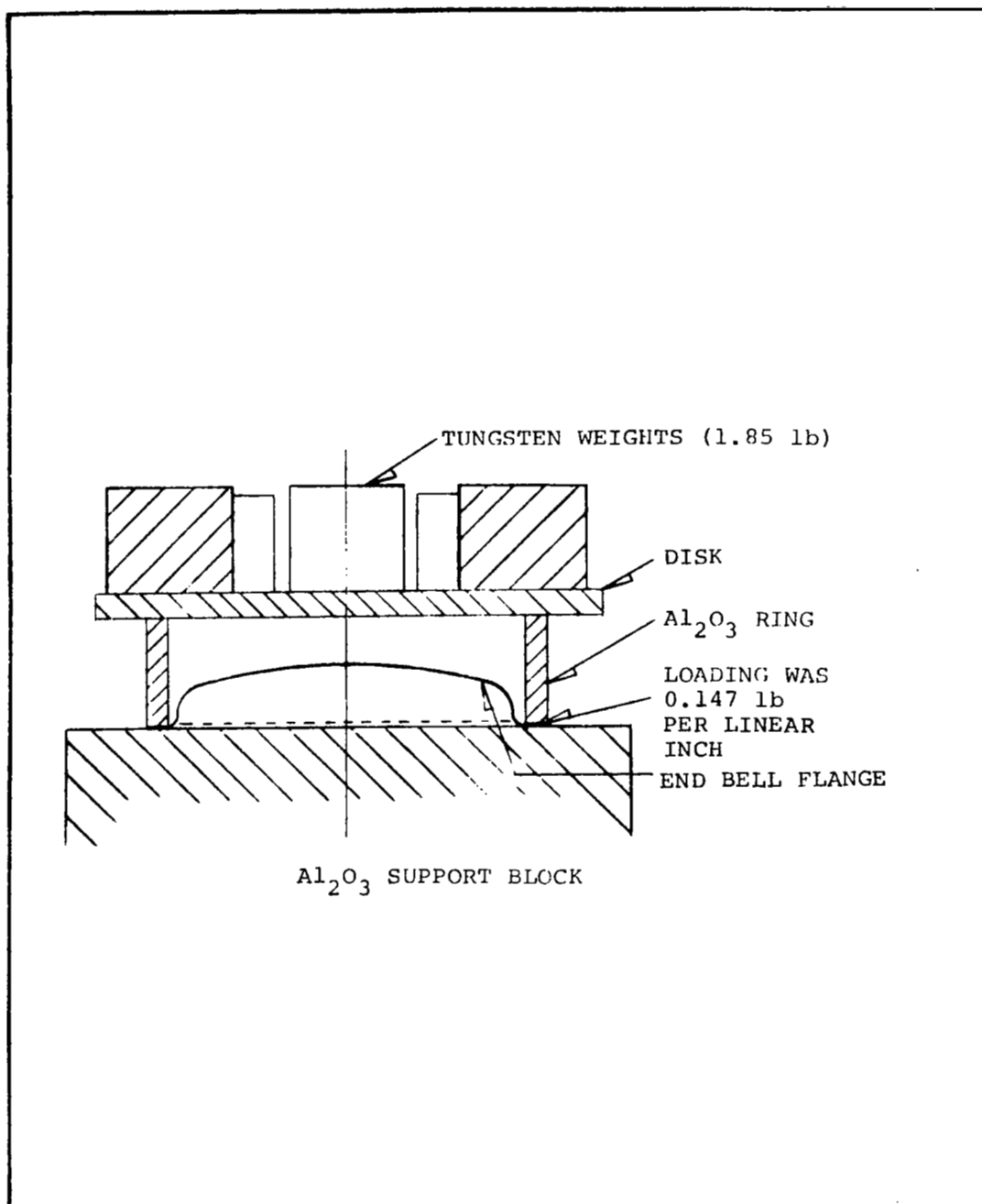
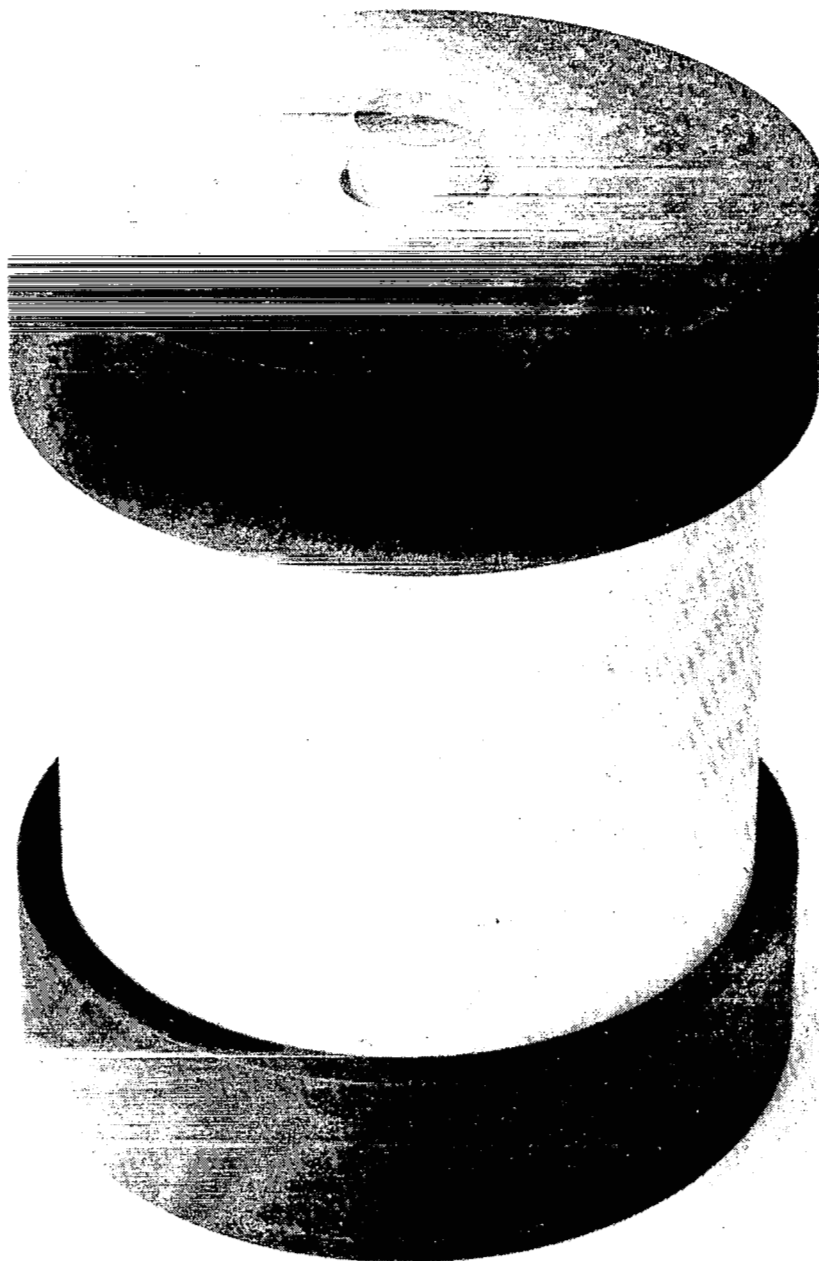


FIGURE II-49. Schematic of End Bell Flange Leveling  
Fixture for the Four-Inch Diameter Model  
Bore Seals




  
ONE INCH

FIGURE II-50. Photograph of Four-Inch Diameter Model Bore Seal in the Brazing Fixture



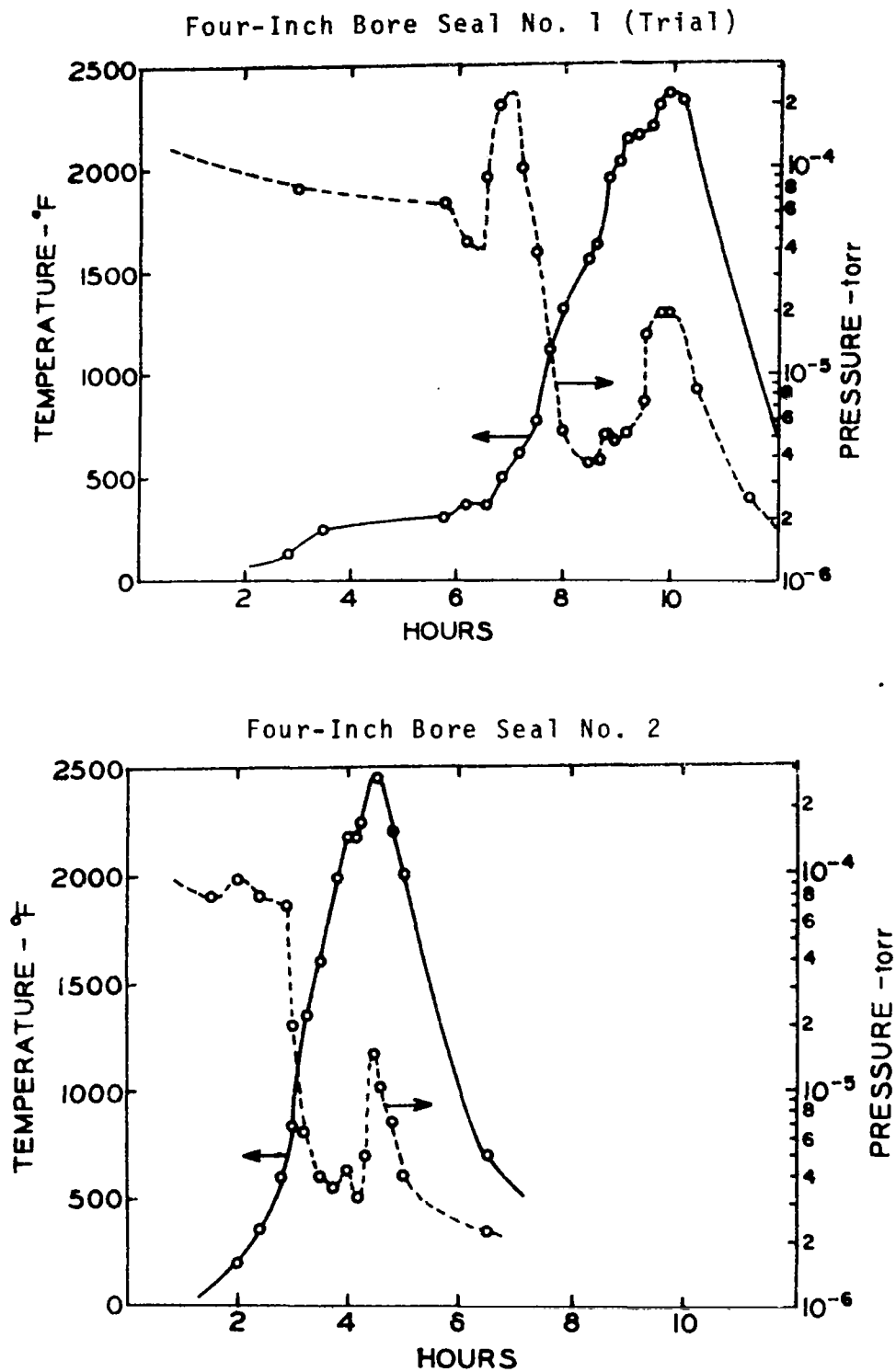


FIGURE II-51. Time-Temperature Brazing Curves of Thermalox 998 (99.8% BeO) - (Cb-1Zr) Model Bore Seals No. 1 and 2 Using Active Brazing Alloy 60Zr-25V-15Cb and Molybdenum Metallizing

by a trial run (with no brazing alloy, but using the same components) to insure that the desired time-temperature profile could be achieved.

Examination of the bore seal after brazing indicated that a good braze had been made, although a generous amount of alloy had been used. The alloy also appeared grainy in spots, as if complete melting had not been achieved. Good, even filleting on the outside of the seal was noted with a negligible amount of alloy flowing onto the outer wall of the ceramic (figure II-52).

Since a rejected ceramic cylinder was used for this trial run, the leak tightness of the seal was uncertain. The leak rate after brazing was the same as that of the ceramic alone. The brazed bore seal was filled with dye and placed in the vacuum-pressure test apparatus. Dye penetrated at two points (figure II-52), previously shown to be the approximate point of leakage of the ceramic before brazing.

#### (2) Four-Inch Bore Seal Capsule No. 2

A welded and back-brazed top end bell was used in this assembly. Ceramic-to-metal brazing was performed as for bore seal No. 1 except that less brazing alloy was used. In addition, the brazing temperature was raised to 2462° F to obtain a more complete melt.

After brazing, the joints exhibited even filleting with no excess or deficiency of alloy evident. Melting appeared to be complete and no further changes in procedure appeared to be necessary for subsequent brazing of 4-inch bore seals.

#### (3) Four-Inch Bore Seal Capsule No. 3

The same procedure and brazing temperature was applied on bore seal No. 3 as had been used for bore seal No. 2. Although the flange on the metal end members had been flattened by the same procedure that had been applied on the flanges for the first two model bore seals, the flange on one end of bore seal No. 3 warped slightly during brazing. Bore seal No. 3 was not vacuum leak tight.

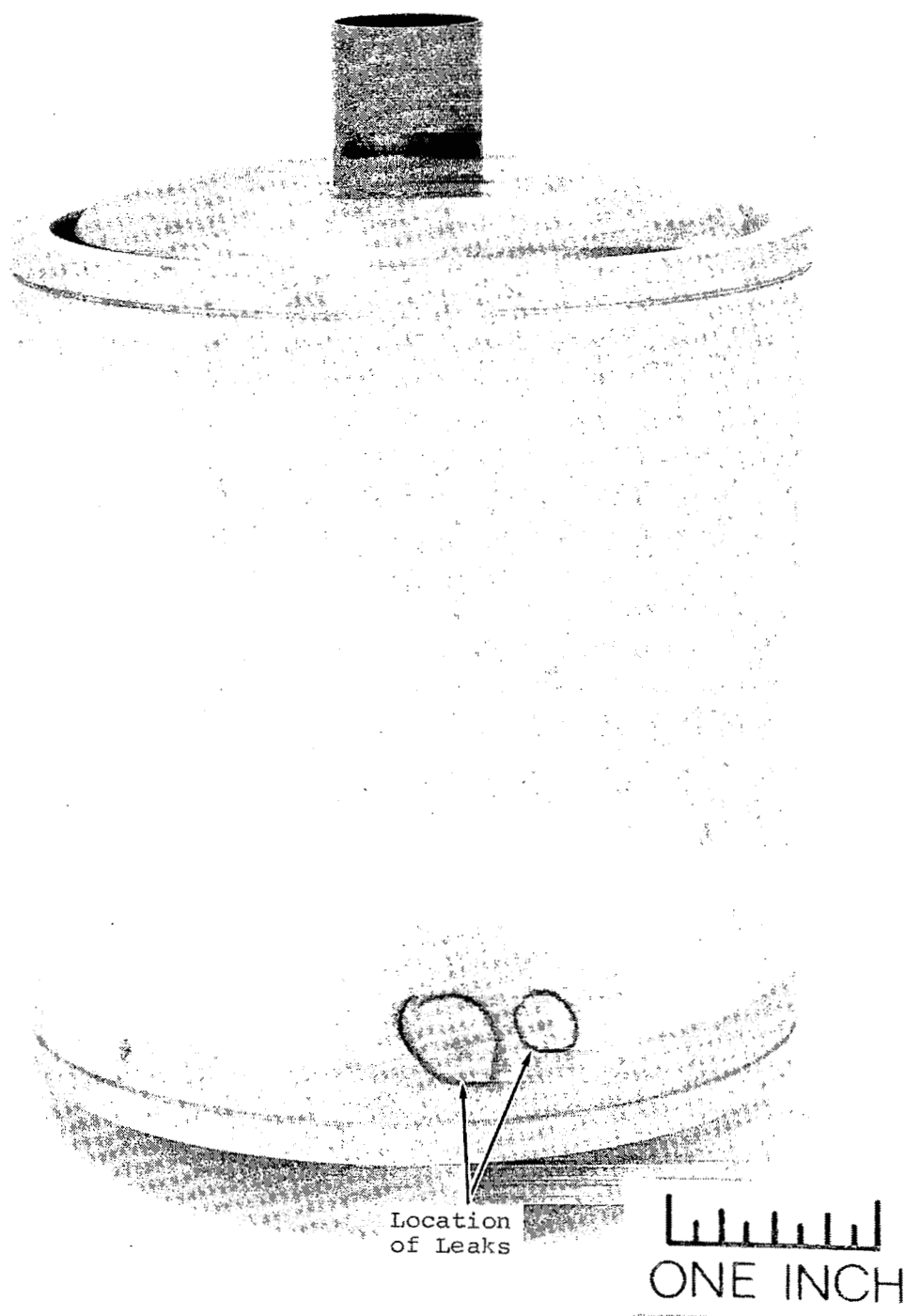


FIGURE II-52. Photograph of Thermalox 998 (99.8% BeO) - (Cb-1Zr) Brazed Bore Seal Capsule No. 1

#### (4) Four-Inch Bore Seal Capsule Nos. 4 and 5

Bore seal capsule No. 4 was brazed with braze alloy 60Zr-25V-15Cb at 2462° F. A back-brazed end bell was used. A good braze joint was obtained although the braze fillet on the inside surface of the back-up ring was heavier than in the first two bore seal capsules.

The brazing results on bore seal capsule No. 5 were the same as that obtained on bore seal No. 4. The Cb-1Zr tubulation was electron-beam welded to the Cb-1Zr end bell as before, but was not back-brazed.

#### f. INSPECTION AND TESTING

The following post-brazing inspection and testing procedure was devised for the 4-inch model bore seal capsules.

Brazed joints were inspected under the stereo-microscope for completeness of melting and for proper amount of brazing alloy. The brazed seal was mounted in a cold vacuum pressure test apparatus (figure II-53). This apparatus consisted of a vacuum chamber attached to and evacuated by the vacuum system of a Veeco helium mass spectrograph leak detector. The bore seal assembly was suspended from the top flange so that when the chamber was evacuated a 15 psi differential pressure existed from the inside to the outside of the bore seal. This simulates the pressure distribution that was expected in operation. Also, the pressure differential must be applied in this way because the Cb-1Zr end members were too thin to withstand the opposite differential without buckling. Helium gas was injected into the bore seal to check leakage.

Bore Seal No. 2 passed the above test on the second try. A leak indication obtained on the first try was traced to the tubing clamped to the bore seal tubulation. The leak was found by filling the bore seal with the dye solution as for bore seal No. 1.

Bore seals Nos. 4 and 5 were leak-tight; no leak being detectable at a sensitivity of  $10^{-9}$  atm - cc/sec.

Bore seal capsules were prepared for filling with potassium by cleaning, as follows:

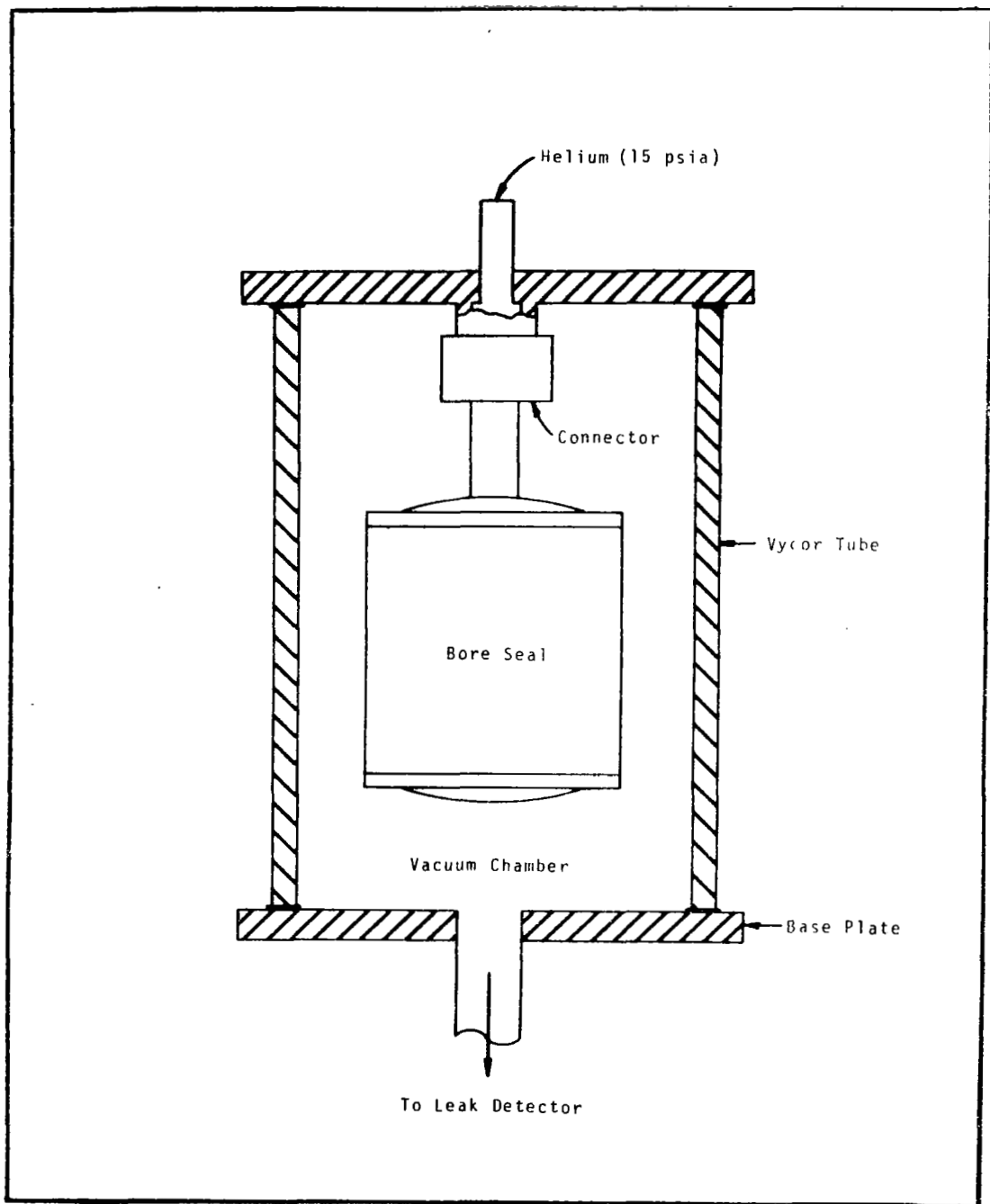


FIGURE II-53. Schematic of a Four-Inch Diameter Model 99.8% BeO - (Cb-1Zr) Bore Seal in Room Temperature Vacuum/Pressure Testing Apparatus

- 1) The dye, which had been used for inspection, was washed out with acetone and the bore seal was air dried.
- 2) Stains were removed from the outside of the ceramic by liquid honing.
- 3) Stains on the Cb-1Zr metal members were removed with brief exposure to 40 parts  $\text{HNO}_3$ , 10 parts HF.
- 4) The bore seal assembly was baked out at  $1470^\circ \text{F}$  for one hour at a pressure of  $<5 \times 10^{-6}$  torr.

Just prior to placement in the electron-beam welding chamber, bore seal No. 4 was fired for 10 minutes at  $1470^\circ \text{F}$  at a pressure less than  $5 \times 10^{-6}$  torr. Bore seal No. 4 was included for potassium loading with a group of Cb-1Zr test capsules used for holding modulus-of-rupture test specimens. About four grams of potassium was put in this bore seal capsule and the closure was made by electron-beam welding. This model bore seal capsule (No. 4) was used in the stator endurance test (ref. II-2). The assembly is shown in figure II-54.

#### g. EVALUATION OF FOUR-INCH BORE SEAL CAPSULE NO. 1

A subtask was started to evaluate the strength and potassium corrosion resistance of the ceramics used to manufacture the 4-inch model bore seal capsules. This was motivated by the questionable visual appearance of the ceramics discussed in Section II-C.8.b.

An outline of the subtask is given below:

- 1) Twenty modulus-of-rupture bars and two ceramic/metal seal samples were cut from 4-inch diameter trial braze bore seal capsule No. 1.
- 2) Five modulus-of-rupture bars were tested in a potassium compatibility capsule and five in a vacuum capsule for 500 hours at  $1600^\circ \text{F}$ .
- 3) After exposure, the twenty bars were tested to determine the as-fabricated strength in the longitudinal direction and as-fabricated strength in the circumferential direction.

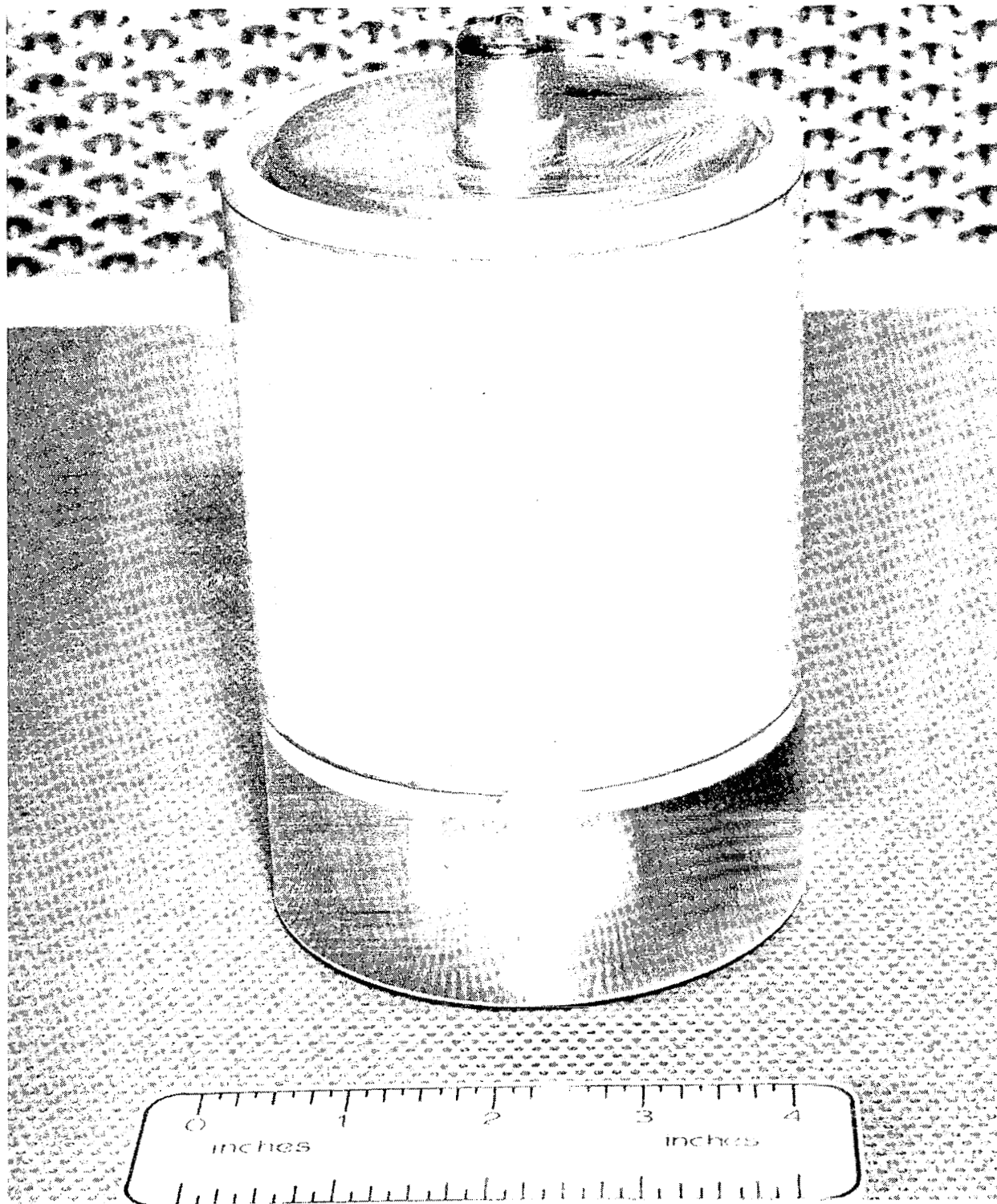


FIGURE II-54. Photograph of Thermalox 998 (99.8% BeO)-(Cb-1Zr) Bore Seal Capsule No. 4 Brazed with 60Zr-25V-15Cb Alloy. (This bore seal, containing potassium, was used in the stator endurance test.)

Modulus-of-rupture bars were cut in an axial direction from the 0.1-inch-thick section of the 4-inch cylindrical ceramic tube. They were then diamond ground to a square cross section. Because of the radius of curvature of the cylinder, it was necessary that the finished bars be slightly smaller than the standard 0.1-inch by 0.1-inch bars normally used on this program. The bars were cleaned and clean-fired in the same manner as the normal ceramic modulus-of-rupture bars. Ten bars were selected at random for loading into capsules and testing as described in Section II-C.6. Two samples sectioned from the seal area were polished. One was inserted in a Cb-1Zr capsule for potassium vapor exposure at 1600° F for 500 hours.

After testing, the five bars exposed to potassium vapor had turned gray in color but no other visible effects were noted. No changes in the vacuum exposed samples were noted.

All of the modulus-of-rupture bars were tested. Results are shown in table II-20. This ceramic appeared to be slightly stronger than other lots of BeO received during the past two years, although this may reflect the slightly smaller size of the bars (see Appendix C).

The strength compares to that of bars that have been brazed above the normal brazing temperature. It was postulated that the higher post-braze strengths could be the result of a heat treatment effect. Possibly the same effect is being shown here. No pre-brazed specimens from the 4-inch diameter cylinders were available.

There was also less degradation in flexural strength than for lot BeO-E used in the earlier 500-hour potassium compatibility run. No significant difference in strength between the longitudinal and circumferential directions was noted.

The potassium exposed specimen of the seal area from bore seal No. 1 and of the matching unexposed specimen were mounted and polished for metallographic examination. Micrographs of these specimens are shown in figure II-39. Four significant features were noted:

- 1) The as-brazed ceramic was cracked near the inside surface of the cylinder in a direction indicating radial tensile forces on the ceramic. The cracks apparently formed after cooling, since one crack in the seal specimen put on test in the potassium test capsule extended



TABLE II-20. Effect of 500-Hour, 1600°F Exposure to Potassium or Vacuum on the Room Temperature Flexural Strength of Beryllia Sectioned from Four-Inch Bore Seal No. 1.

Ceramic Body (a)	Key	Room Temperature Flexural Strength (c) of Unexposed (d) Specimens (psi)	Room Temperature Flexural Strength (c) After Specified Exposure for 500 Hours at 1600°F (psi)	
			Potassium Vapor	Vacuum
Approximately 0.1-inch square sections cut from 4-inch diameter 99.8% BeO bore seal, longitudinal direction	$\bar{x}$ s n	24,700 3,400 5		23,600 2,900 5
Approximately 0.1-inch square section cut from 4-inch diameter 99.8% BeO bore seal, circumferential direction	$\bar{x}$ s n	24,800 2,700 5	20,100 2,200 5	
Thermalox 998 Beryllia (b) (99.8% BeO) Lot EA (e)	$\bar{x}$ s n	20,900 2,160 5		
Thermalox 998 Beryllia (b) (99.8% BeO) Lot B (e)	$\bar{x}$ s n	21,100 2,500 3		
Thermalox 998 Beryllia (b) (99.8% BeO) Lot E (e)	$\bar{x}$ s n	19,820 1,420 5	15,800 200 4	
<p>Key: <math>\bar{x}</math> = arithmetic mean s = standard deviation n = number tested</p> <p>(a) See Appendix B for composition. (b) Modulus-of-rupture bars 0.1 inch x 0.1 inch x 1 inch. (c) All tests made by four point loading at a load rate of 0.1 inch per minute. (d) Specimens unexposed but in the as-brazed condition, after brazing with 60Zr-25V-15Cb alloy. (e) For comparison.</p>				

through the two-phase exfoliated region and stopped at the edge of the (apparently) ductile, light-colored brazing alloy.

- 2) The ceramic had exfoliated at the corners where excess brazing alloy had flowed out of the joint. The dark phase surrounded by the white brazing alloy appeared to be a different shade from the base ceramic, but visual examination at high magnification showed the same fine porous structure to exist in both places. Also, no difference in shading was noted visually.
- 3) The ceramic had reacted with the brazing alloy along the entire joint face and small particles of BeO were suspended in the reaction layer.
- 4) The Cb-12Zr had been taken into solution by the brazing alloy until the undisturbed sheet was only 8 to 10 mils in thickness at the inside edge of the ceramic.

It is apparent that an overbrazed condition existed, but despite that, a strong, vacuum-tight joint was made. The above conditions were not noted in smaller brazed structures. This produces some insight into the problems that will exist when larger systems are fabricated.

The following improvements are indicated for future application of active metal brazing to large structures:

- 1) Careful control should be maintained over the amount of brazing alloy applied in order to prevent "puddling" or other formation of excess alloy at the inside surface of the back-up ring. This is very difficult using the present powder form of the brazing alloy. A method of controlling the amount per unit seal area needs to be perfected.
- 2) Reduced time and/or temperature in the liquid condition is required. In order that findings obtained from small assemblies can be properly utilized, the brazing cycle must be programmed to resemble that obtainable with large structures in a larger vacuum furnace.

It is concluded from work in this task, and other work, that the 4-inch by 4-inch bore seals are suitable for preliminary testing and that scaling-up to larger assemblies can be considered. However, it is clear that the following limitations exist:

- 1) The brazing cycle for large structures is not yet optimum. The brazing alloy appears to have a wide latitude in time-temperature conditions above the melting point as far as producing strong, vacuum-tight joints is concerned, but no data exist on the potassium compatibility and metallurgical stability of the structures obtained under the different brazing conditions.
- 2) The form of the alloy and the method of applying it is not yet adequate to control the uniformity of the brazed joint to the desired level. It is believed that the surface cracking observed is related to this problem.
- 3) The increasing mismatch between the thermal expansion of metal and ceramic at the brazing temperature as larger assemblies are brazed is expected to magnify difficulties that appear minor on present sized assemblies. The effect may be to greatly narrow the latitude that the brazing alloy now exhibits. To minimize the supplementary effort needed when these difficulties arise, it is important to recognize that increased control over the manufacturing process is needed to obtain a meaningful experimental comparison.
- 4) The large ceramics appear to have uneven density and to have inadequate quality control during manufacture. The surface porosity and appearance, which gave rise to earlier concern, may be functions primarily of the specimen size. No meaningful non-destructive acceptance tests have been developed.

#### D. CONCLUSIONS

- 1) High strength, vacuum tight beryllia-to-Cb-1Zr joints have been made with the active-metal brazing alloy having a composition in weight percent of 60Zr-25V-15Cb. Joints made at a brazing temperature of 2460° F have exhibited an average room temperature flexural strength of 22,000 psi and high tab-peel strength (ductile, high-shear strength). Modulus-of-rupture assemblies in the as-brazed condition retain their strength through 1600° F.
- 2) Thermalox 998 (99.8% BeO) bodies fabricated by isostatic pressing and sintering, although slightly more porous than desired, retain high-flexural strength after 2000

hours exposure to potassium vapor at 1600° F. The ceramic (alone, without brazing) also retained high flexural strength after 1500-hours exposure to lithium at 1600° F.

- 3) Ceramic bodies which have been subjected to the standard 30-minute "clean fire" at 2597° F in a mixture of 75%N<sub>2</sub>-25%H<sub>2</sub> and 10 minutes at 1832° F in vacuum ( $<5 \times 10^{-6}$  torr) show very low outgassing rates of oxygen-containing gases. Ceramics treated in this manner limit the contamination of alkali-metal-cooled space electric power systems.
- 4) Ceramic-to-metal seal systems fabricated with 60Zr-25V-15Cb brazing alloy utilizing Thermalox 998 (99.8% beryllia) and a Cb-1Zr metal member show adequate strength after 2000-hour 1600° F exposure to potassium vapor, but greater deterioration in strength after exposure to liquid potassium or lithium.
- 5) A four-inch diameter Thermalox 998 (99.8% beryllia)-Cb-1Zr model bore seal brazed with this brazing alloy remained potassium leak-tight after 5000 hours at 1300° F in a thermal-ultra high vacuum chamber.



## APPENDIXES

These appendixes contain supplementary information in the areas of material procurement, manufacturing and process procedures, and materials analyses. This information will define only those areas necessary for the proper performance of each individual material or component. Procurement or purchasing specifications are used only to establish product quality and product reproducibility. The process information documents, however, provide the detail information necessary for the fabrication and assembly of each component.

APPENDIX A  
SPECIFICATIONS

- I. Procurement Information
- II. Manufacturing Procedures

## I. PROCUREMENT INFORMATION

### Introduction

The first section of this Appendix contains procurement information which defines the various qualities required in raw and finished materials. The method of preparation of manufacture is not controlled, but the product must meet specified requirements to be acceptable for further processing or final use.



PROCUREMENT INFORMATION FOR COLUMBIUM - 1 PERCENT ZIRCONIUM ALLOY  
SCOPE

- 1.1 Scope This specification covers Columbium-1 percent Zirconium Alloy in sheet form intended for explosive bonding, high temperature structural applications and use in alkali metal environments.

2. APPLICABLE DOCUMENTS

- 2.1 Government Documents None

- 2.2 Non-Government Documents

ASTM Designation E8-57T	Method of Tension Testing of Metallic Materials
ASTM Designation E29-58T	Recommended Practices for Designating Significant Places in Specified Limiting Values.
ASTM Designation (Pending)	Methods for Chemical Analysis of Reactor and Commercial Columbium
ASTM E112-61	Estimating Average Grain Size of Metals
AMS2242	Tolerances, Corrosion and Heat Resistant Sheet, Strip, and Plate
AMS2645	Fluorescent Penetrant Inspection
MAB-M6-M	Evaluation Test Methods for Refractory Metal Sheet Materials

3. REQUIREMENTS

- 3.1 Acknowledgments The vendor shall mention this document in all quotations and all Purchase Order acknowledgments.
- 3.2 Manufacture Material covered by this document shall be made from ingots which have been at least double vacuum melted by the electron beam method. Breakdown operations shall be performed with metal working equipment normally found in primary ferrous and non-ferrous plants.
- 3.3 Processing The starting stock size, processing temperatures, reductions, in-process annealing cycles shall be selected by the vendor to achieve the grain size range specified in Paragraph 3.6 and the mechanical properties specified in Paragraph 3.7.
- 3.4 Condition
- 3.4.1 General The finished sheet shall be supplied in the recrystallized condition throughout the cross-sectional area

to the grain size range specified in Paragraph 3.6.

- 3.4.2 Heat Treatment: All annealing shall be carried out at a pressure no greater than  $1 \times 10^{-5}$  torr. All sheet to be annealed shall be thoroughly degreased and chemically cleaned. The conditions of final annealing shall be reported in the certificate of compliance.
- 3.4.3 All material shall be free of contamination or internal oxidation. After the final heat treatment the material shall be examined metallographically for evidence of possible contamination caused by unsatisfactory heat treating atmospheres or processing conditions. At the discretion of the buyer, samples taken to include at least one surface of the final product, and not exceeding 0.050 inch thick may be chemically analyzed by the purchaser for oxygen, nitrogen, hydrogen and carbon. The analysis shall not exceed the limits set forth in Paragraph 3.5.3. Contamination above the limits of Paragraph 3.5.3 shall be cause for rejection of all material represented by that sample.

### 3.5 Chemical Composition

- 3.5.1 Ingot/Billet Composition: The chemical composition of ingots and billets for conversion to finished sheet shall conform to the analysis listed in the following table.

TABLE I  
CHEMICAL COMPOSITION  
COLUMBIUM-1 PERCENT ZIRCONIUM ALLOY

<u>Element</u>	<u>Minimum Content</u>	<u>Maximum Content</u>
Carbon		100 PPM
Nitrogen		75 PPM
Oxygen		100 PPM
Hydrogen		10 PPM
Tantalum		1400 PPM
Molybdenum		1000 PPM
Nickel		100 PPM
Cobalt		50 PPM
Iron		50 PPM
Zirconium	0.80 W/O	1.20 W/O
Columbium	Remainder	

- 3.5.2 Final Product Composition: The manufacturers ingot analysis shall be considered the chemical analysis for the sheet supplied under this document, except that for carbon, oxygen, nitrogen, and hydrogen content, which shall be determined on the finished sheet.

- 3.5.3 Check Analysis: Finished sheet analysis shall not exceed the following limits or variations:

<u>Element</u>	<u>Check Analysis Limits, Max, PPM</u>	<u>Permissible Variations in Check Analysis, PPM</u>
Carbon	100	+ 5
Oxygen	100	+ 5
Nitrogen	75	+10
Hydrogen	10	+ 5

- 3.6 Grain Size The grain size of the final product shall conform to the following limits: minimum grain size of ASTM6 with an allowable spread in anyone item of 2 with 90 percent at a grain size of 6.
- 3.7 Mechanical Properties The final product shall satisfy the following mechanical property requirements:

- 3.7.1 Room Temperature Tensile Properties: Representative samples of the material in final form shall meet the following at a temperature of 65°-85°F. Samples shall be taken transverse to the final rolling direction.

<u>F<sub>TU</sub> (ksi)</u>		<u>F<sub>TY</sub>, (0.20 percent (ksi))</u>		<u>Elongation in 2 Inches (Percent) Min.</u>
<u>Min.</u>	<u>Max.</u>	<u>Min.</u>	<u>Max.</u>	
35	55	20	30	20

- 3.7.2 Bend Ductility: Representative samples of the materials in final form shall withstand the following bend test at room temperature without failure when tested according to procedures described in the most recent revision of the Materials Advisory Board report MAB-176-M, "Evaluation Test Methods for Refractory Metal Sheet Materials." The samples shall be sectioned with the long axis of the bend specimens perpendicular to the final rolling direction.

- 3.7.2.1 Sheet 0.060 inch in thickness and under shall be bent over a 1T radius through 105° at a ram speed of 1 inch per minute and subsequently flattened for a total bend of 180°.

### 3.8 Tolerances

#### 3.8.1 Sheet

- 3.8.1.1 Definition. Sheet includes material 6 inches wide or over and up to 0.187 inch in thickness.

3.8.1.2 Dimensions. Sheet dimensions shall conform to those presented in Table II.

3.8.1.3 Flatness. Total deviation from flatness of sheet and strip shall not exceed 6% as determined by the formula:

$$\frac{H}{L} \times 100 = \% \text{ Flatness Deviation}$$

where: H = maximum distance from a flat reference surface

and: L = minimum distance from this point to the point of contact with the reference surface.

The actual values shall be reported. In determining flatness, the sheet shall not be subject to external pressure at any point but shall lie freely on a flat surface during measurement. Oilcanning will be reported. An estimate of the extent (area, height, etc.,) of these defects shall be made.

3.9 Reports The manufacturer shall supply at least three copies of a report showing non-proprietary manufacturing methods, processing conditions, and test procedures and results for each lot of material in the shipment. The report shall also include the number of the specification and the purchase order or contract number.

TABLE II

DIMENSIONAL TOLERANCES FOR SHEET AND STRIP

<u>Material Thickness, Inch</u>	<u>Width, Inches</u>	<u>Thickness Tolerances, Inch</u>
0.020-0.039	to 24	± 0.0030
<u>Material Thickness, Inch</u>	<u>Width &amp; Length Tolerances, Inch</u>	
0.010-0.059	+ 0.100, -0	

4. MAXIMUM ALLOWABLE DISCONTINUITIES

4.1 General The finished product shall be visibly free from oxide or scale of any nature, grease, oil, residual lubricants, and other extraneous materials. Cracks, laps, seams, gouges and fins shall be unacceptable.

4.2 Porosity and Inclusions Indications of internal porosity and non-metallic inclusions greater than 0.020 inch or 3% of the thickness, whichever is smaller, shall be unacceptable. Those indications in the range 0.010 inch to 0.020 inch or 2% of the thickness, whichever is smaller, shall be a minimum of 0.50 inch apart; those indications less than 0.010 inch shall be a minimum of 0.12 inch apart.

4.3 Surface Rework All surface pores, gouges, and other defects deeper than 0.005 inch or 3% of the thickness, whichever is smaller, shall be unacceptable. Surface imperfections may be faired smooth to remove any notch effect provided dimensional tolerances are still maintained.

## 5. QUALITY ASSURANCE PROVISIONS

5.1 Vendor Responsibility The manufacturer shall make all tests and inspections of the material covered by this specification before shipment, unless otherwise specified. All test and inspection results shall be furnished to the purchaser.

5.2 Sample Selection Care shall be exercised to insure that the samples selected for testing and chemical analyses are representative of the material and uncontaminated by the sampling procedure. Samples for the determination of mechanical properties shall be selected so as to consume a minimum amount of material, i.e., specimens may be taken transverse to the final working direction from sheet. If there is any question about the sampling technique or the analysis, the methods for sampling and analysis shall be those agreed to by the buyer and seller. The location of test samples shall be reported in the certificate of compliance.

### 5.3 Test Methods

5.3.1 Chemical Analysis: Chemical analyses shall be conducted by mutually acceptable procedures, such as the vacuum fusion methods for gases, the combustion method for carbon, and the spectrochemical methods for metallic elements. Disputes shall be settled by accepted referee methods, such as the ASTM "Methods for Chemical Analyses of Reactor and Commercial Columbium."

5.3.2 Tensile Test: The tension test shall be conducted in accordance with ASTM Designation E8-57T, "Methods of Tension Testing of Metallic Materials." Yield strength shall be determined by the offset (0.2%) method. The tensile properties shall be determined using a strain rate of 0.005 inch per inch per minute up to 0.6% offset, and then 0.05 inch, plus or minus 0.02 inch, per inch per minute to fracture.

5.3.3 Grain Size: Grain size determinations shall be made according to ASTM Specification E112-61, "Estimating the Average Grain Size of Metals."

5.4 Number of Test Required Representative test specimens from the finished product representing each ingot and each lot of material shall be taken to determine conformity to this specification. The minimum frequency of these tests shall be:

Finished Product Chemistry - one per lot per ingot  
Tensile Test - one per lot per ingot  
Bend Test - two per lot per ingot  
Grain Size - two per lot per ingot

5.5 Retests and Rework

5.5.1 Surface Contamination: Any sample or specimen exhibiting obvious surface contamination or improper preparation which disqualifies it as a truly representative sample shall be replaced with a new sample.

5.5.2 Rework: If inspection and test results of a lot do not conform to the requirements of this specification, the lot may be reworked at the option of the manufacturer. The lot shall be acceptable if all test results, after reworking, conform to this specification.

5.6 Inspection

5.6.1 Methods of Inspection

5.6.1.1 Ultrasonic. Unless otherwise agreed to by the purchaser and the vendor, the ingot material shall be inspected ultrasonically. The finished sheet shall be tested for defects with a Vidigage and the results reported to the purchaser.

5.6.1.2 Penetrant Inspection. The exterior surface of the product shall be penetrant inspected and found free of flaws as specified in Paragraph 4.3 using AMS 2645, "Fluorescent Penetrant Inspection," or AMS 2646, "Contrast Dye Penetrant Inspection." All parts thus inspected shall be marked with ink stamps as described in the specification; impression stampings or etching shall be unacceptable.

5.6.1.3 Reports. The manufacturer shall supply at least three copies of a report showing inspection results for each lot of material in the shipment. The report shall also include the number of the specification and the purchase order or contract number.

- 5.7 Rejection Material not conforming to this specification or to any authorized modification shall be subject to rejection. Unless otherwise specified, rejected material may be returned to the manufacturer at the manufacturer's expense if the purchaser does not receive other instructions for disposition within three weeks after notice of rejection.
- 5.8 Referee If the manufacturer and the purchaser disagree about the conformance of the material to the requirements of this specification or any special test specified by the purchaser, a mutually acceptable referee's test shall be used to determine conformance.

## 6. PREPARATION FOR DELIVERY

- 6.1 Identification Each bundle, box or carton shall be legibly and conspicuously marked or tagged with the number of this specification, purchase order, or contract number, type, ingot number, lot number, nominal size, and the gross, net, and tare weights. When each bundle, box or carton consists of components from more than one ingot number or lot number, each component shall be identified individually.
- 6.2 Packing Each individual sheet shall be wrapped in heavy gauge polyethylene film or other similar material and packed in a manner assuring safe delivery when properly transported by any common carrier. The surfaces of each sheet shall be covered with a strippable adhesive backed protective film or paper.

## 7. DEFINITION

- 7.1 Lot A lot shall include all material of the same size, shape, condition and finish from one heat of material and which has received the same processing, has been annealed in the same vacuum annealing charge and has been processed simultaneously in all operations in which temperatures may reach 500°F or above. When process temperatures and environments are closely controlled or when closely adjacent sizes receive similar processing, lots may be combined for chemical, tensile and stress-rupture tests only, provided prior written approval has been obtained from the purchaser.
- 7.2 Check Analysis An analysis may be requested by the purchaser of the metal after it has been processed into finished mill forms, to verify the composition within a heat or lot. Check analysis tolerances do not broaden the specified heat analysis requirements but rather cover variations between laboratories in the measurement of the chemical content.
- 7.3 Significance of Numerical Limits For determining compliance with the specified limits for requirements of the properties listed below, an observed value or a calculated value shall be rounded off

using the rounding-off method in ASTM Designation E29-58T, "Recommended Practices for Designating Significant Places in Specified Limiting Values."

<u>Test</u>	<u>Rounded-Off Unit for Observed or Calculated Value</u>
Chemical composition and dimensional tolerances (when expressed decimally)	Nearest unit in the last right- hand place of figures of the specified limit
Tensile strength	Nearest 100 psi
Elongation	Nearest 1%



## Procurement Information for Beryllium Oxide Ceramic Parts

### NOTE: IMPORTANT

BECAUSE OF THE POTENTIAL HEALTH HAZARD ASSOCIATED WITH BERYLLIUM OXIDE DUSTS AND VAPORS, ALL PARTS SUPPLIED UNDER THIS SPECIFICATION MUST BE ABSOLUTELY FREE FROM ANY TRACE OF BERYLLIUM OXIDE DUST OR FREE UNBONDED PARTICLES.

1. This document covers high purity, high density beryllium oxide parts for application as electrical insulation and for containing alkali metals in elevated temperature electrical apparatus.

Note: Unless otherwise specified, the following requirements apply to all items.

2. No change shall be made in the quality of successive shipments of material furnished under this document without first obtaining the approval of the purchaser.

### MANUFACTURE

3. The parts shall be made according to the supplied drawing by the techniques of powder metallurgy using the appropriate presses and furnaces.

### COMPOSITION

4. The finished parts shall meet the following composition limits specified on the drawing as follows:

#### Composition

Aluminum	150	ppm	max.
Iron	100	ppm	max.
Silicon	50	ppm	max.
Calcium	80	ppm	max.
MgO	1000	ppm	max.
Silver	30	ppm	max.
Copper	30	ppm	max.
Chromium	30	ppm	max.
Manganese	30	ppm	max.
Molybdenum	30	ppm	max.
Sodium	30	ppm	max.
Nickel	30	ppm	max.
Zinc	30	ppm	max.
Boron	10	ppm	max.
Cadmium	10	ppm	max.
Cobalt	10	ppm	max.

#### Composition

Potassium	10	ppm	max.
Lithium	10	ppm	max.
Lead	10	ppm	max.
BeO	99.8		min.

#### DENSITY

5. The parts shall have a uniform density within the limits specified below.

2.84 to 2.92 g/cc

#### CONDITION AND APPEARANCE

6. All parts shall be clean , white and free of surface discoloration, finger prints or surface contamination.
7. All parts shall be free of chips, nicks, scratches, cracks and other deleterious imperfections as determined by visual techniques and the techniques of die penetrant inspection.
8. Each part shall conform to the drawing supplied with regard to dimensions and surface finish.

#### PROPERTIES AND TESTS

9. A certified chemical analysis of a representative sample from each material lot and shipment shall be supplied.
10. Density, as determined by fluid displacement, shall be supplied on at least two (2) representative samples from each geometrical configuration from each shipment.

#### PACKAGING

11. Unless otherwise specified, the parts shall be packaged in clean plastic airtight packages and protected from contamination and breakage due to handling.
12. Each shipping carton shall be marked with the name of the manufacturer, purchase order number and weight.

## Procurement Information for Ceramic Braze Alloy

1. This document covers the procurement of one braze alloy used for ceramic-to-metal joints.
2. No change shall be made in the quality of successive shipments of material furnished under this specification without first obtaining the approval of the purchaser.

### APPROVED SUPPLIERS

3. Battelle Memorial Institute, Columbus, Ohio 43201, has been the primary supplier; other sources equipped to maintain composition and purity could be used.

### MANUFACTURE

4. The final material shall be in powder form and have the following composition: 60Zr-25V-15Cb. High purity, low interstitial raw materials shall be used in melting the braze alloy constituent materials. The alloy shall be melted 4-6 times (by the inert-gas nonconsumable arc-melting technique or equivalent method) to obtain a pure alloy button. The button shall be turned into chips on a small lathe, and the chips then reduced to powder in a diamond mortar, or by using equivalent methods which maintain alloy purity. Powder shall be 100% minus 50 mesh.

### PACKAGING

5. The powder shall be packed in sealed containers to prevent contamination from external sources.
6. Each shipping container shall be marked with the name of the manufacturer, purchase order number, and quantity of material.

## II. MANUFACTURING PROCEDURES

### Introduction

This section of Appendix A contains processing specifications for brazing and cleaning using materials which have previously met the procurement specification requirements.

## MANUFACTURING PROCEDURE FOR CERAMIC-TO-METAL BRAZING

### 1. Dye Check Procedure

#### 1.1 OBJECTIVE:

To aid in the inspection of incoming raw ceramics for chips, scratches, pits, pocks, cracks, porosity, etc.

#### 1.2 PROCEDURE:

1.2.1 Dip in Rhodamine B solution

1.2.2 Hot tap water rinse

1.2.3 Two methyl alcohol rinses.

1.2.4 Dry and inspect.

### 2. Ceramic Cleaning Procedure

#### 2.1 OBJECTIVE:

The purpose of this procedure is to assure that all foreign matter is removed from ceramic rings and cylinders prior to metallizing or brazing.

#### 2.2 PRECAUTIONS:

After this cleaning procedure has been started, ceramic parts shall not be handled with the bare hands. Regular Wilson Natural Latex Industrial gloves are to be used. Air hoses are not to be used for drying ceramic parts. Routing tags and other identification tags should not be placed where the ink, dye, or other substances from them might contaminate the ceramic parts. The practice of stacking ceramics one on the other must be avoided as this tends to chip and otherwise damage them.

#### 2.3 PROCEDURE:

- 2.3.1 Immerse the ceramic for 15 to 20 minutes in detergent solution "A" (Triton X100) which is maintained at a temperature of  $131^{\circ} \pm 5^{\circ} \text{F}$  ( $55^{\circ} \pm 3^{\circ} \text{C}$ ).
- 2.3.2 The ceramic parts should be rotated or agitated several times during the period of immersion.
- 2.3.3 Remove the parts from the detergent solution and scrub with a nylon brush and detergent solution. Step 3 applies to the larger (3-4 inch diameter) size ceramic cylinders.
- 2.3.4 Rinse the ceramic part thoroughly in hot running water.
- 2.3.5 Rinse the ceramic part thoroughly in running de-ionized water.
- 2.3.6 Rinse the ceramic part in a shallow container of acetone by rotating the part on its side. NOTE: Discard the acetone after rinsing each ceramic part (large ceramic parts only).
- 2.3.7 Rinse in fresh acetone as in Step 6. This acetone may be used as the first acetone rinse for the next ceramic.
- 2.3.8 Place the ceramic on clean tissue and allow to thoroughly dry. NOTE: If the parts are to be stored, they should be wrapped in a double thickness of tissue. Large ceramic parts should be wrapped individually.

### 3. Procedure for Ceramic Metallizing (Alternate Method of Preparation)

#### 3.1 OBJECTIVE:

To provide an interface layer on the ceramic which is more readily wet by the active metal braze. With some braze alloys, the metallizing improves the strength of the brazed joint.

#### 3.2 PROCEDURE:

- 3.2.1 Mask the cleaned ceramic areas adjacent to the surface to be metallized with five mil thick molybdenum foil.
- 3.2.2 Mount the ceramic on a turntable in the metallizing apparatus, as shown in Figure I.
- 3.2.3 Wrap sufficient five mil molybdenum wire on the tungsten filament to provide a metallized layer greater than one micron thick.

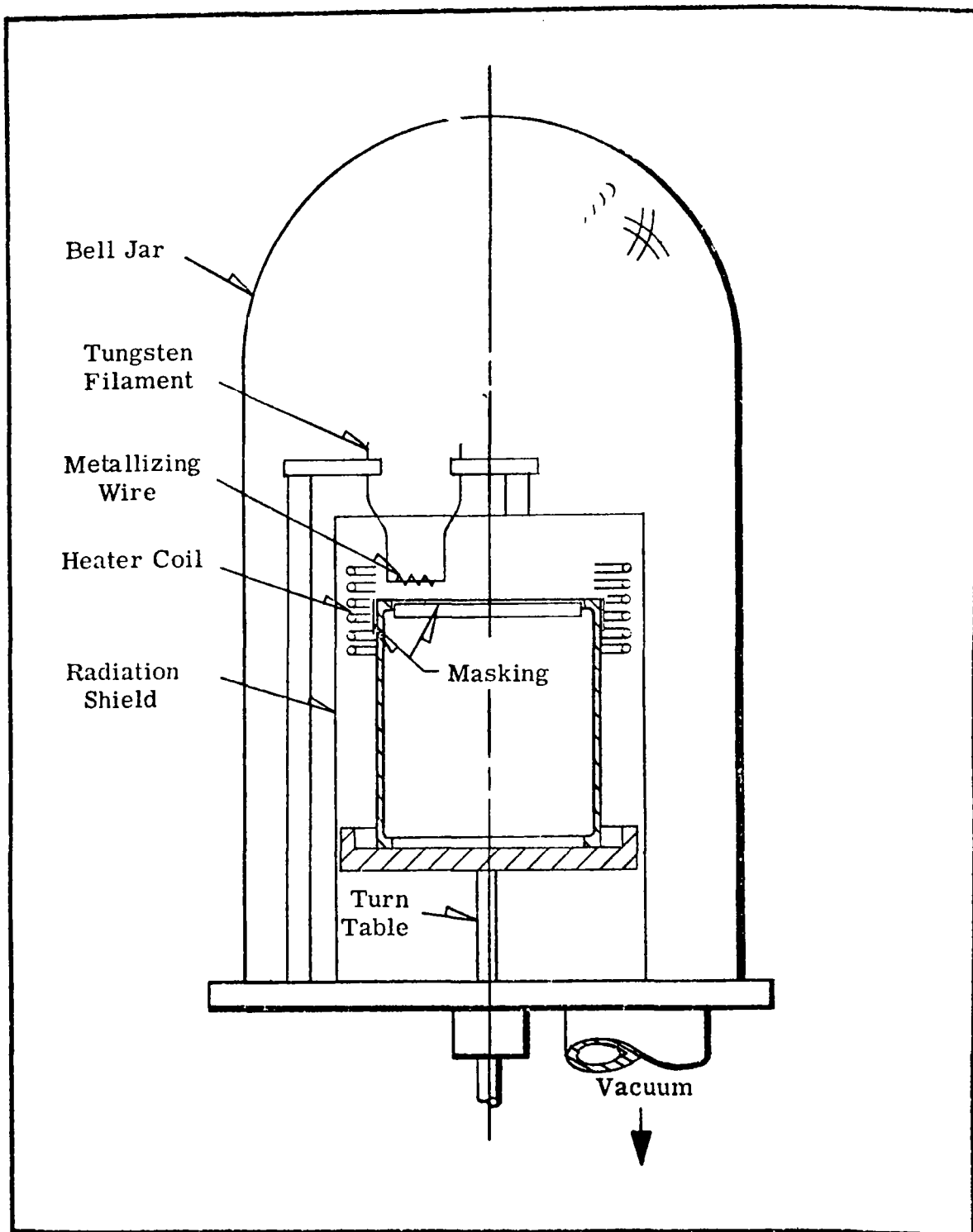


FIGURE I Schematic of Ceramic Metallizing Apparatus

- 3.2.4 Evacuate the metallizing apparatus to less than  $5 \times 10^{-6}$  torr and then heat the ceramic to above  $932^{\circ}\text{F}$ .
- 3.2.5 Evaporate the molybdenum onto the ceramic as it is rotated at six rpm.
- 3.2.6 Bring the apparatus to room temperature before opening the chamber to ambient pressure.

#### 4. Procedure for the Application of Active Metal Brazing Alloy

##### 4.1 OBJECTIVE:

To increase uniformity of braze joint thickness.

##### 4.2 PROCEDURE:

- 4.2.1 Clean and/or fire all required parts by appropriate cleaning procedure and store in suitable containers to maintain cleanliness until use.
- 4.2.2 Utilize clean work area for assembly. For large assemblies which require over five minutes to prepare, use a laminar-flow assembly bench.
- 4.2.3 Utilize clean assembly techniques, clean gloves, finger cots, tools and jigs, clean and dust-free work surface, etc.
- 4.2.4 Apply braze alloy to joint area by method 4.2.4.1 or 4.2.4.2 below.
  - 4.2.4.1 Powder form: Suspend powder (  $< 50$  mesh) in Butyl Methacrylate lacquer.

360g Butyl Methacrylate (Lucite #44)  
1500g Butyl Alcohol (C.P.)  
1500g Butyl Acetate (C.P.)

Apply evenly to appropriate ceramic surface(s) with small spatula at approximately 0.5g per square inch.
  - 4.2.4.2 Foil form: Cut foil (normally 0.002-0.004 inch thick) to exact seal area geometry, or as dictated by foil thickness and experience. Place in seal area. Tack in place with methacrylate lacquer, if necessary.
- 4.2.5 Assemble ceramic and metal parts for brazing in appropriate clean braze jig and put weights in position if required. (The fixture used on this program weighed 0.25 pound and the tungsten weights weighed 1.23 pound.) Normally, molybdenum or tungsten weights are to be used. Record the type and size of weights in the Brazing Log Book.



4.2.6 • Place jigs containing unbrazed assemblies in vacuum brazing furnace chamber and check part alignment and weight position before closing furnace.

4.2.7 Record alloy composition, form, and weight of alloy used in the Brazing Log Book.

5. Vacuum Brazing Procedure

5.1 OBJECTIVE:

To insure reproducibility of the brazing cycle.

5.2 PROCEDURE: \*

5.2.1 Load the vacuum furnace with the same number and distribution of parts and jigs as was used in the original time-temperature determination for a specific alloy.

5.2.2 Close the furnace, bell jar, etc., and slowly raise temperature, keeping pressure below  $5 \times 10^{-5}$  torr.

5.2.3 Fill out Brazing Log Sheet and maintain time, temperature and vacuum log.

5.2.4 Hold the temperature for 10 minutes at  $180^{\circ}\text{F}$  below brazing temperature to allow the furnace to reach equilibrium at  $1 \times 10^{-5}$  torr.

5.2.5 Increase the temperature rapidly to the brazing temperature and hold for five minutes. Monitor the temperature closely.

5.2.6 Allow the parts to cool to  $400^{\circ}\text{F}$  or less in vacuum, then backfill with helium.

5.2.7 Allow the parts to cool 15 minutes in helium before opening the furnace.

5.2.8 Complete Brazing Log information.

- All brazing temperatures monitored using a Pt-Pt-10%Rh thermocouple. An optical pyrometer (not corrected for emissivity) was utilized to verify specimen brazing temperatures.

## Procedure for Cleaning Columbium-1% Zirconium Alloy

1. Follow the procedures specified herein.

2. OBJECTIVE:

2.1 To clean Columbium-1% Zirconium alloy prior to tungsten inert gas or electron beam welding, or vacuum firing or brazing.

PRECAUTION: The cleaning fluid is an extremely hazardous cleaning solution. Use suitable precautions.

3. PROCEDURE:

3.1 Degrease parts, rinse and dry.

3.2 Totally immerse parts in 100°-125°F solution of:

Hydrofluoric acid (48% solution)	20% by volume
Nitric acid (70% solution)	20% by volume
Water	60% by volume

(Immersion time as required for desired stock removal.)

3.3 Rinse in tap water.

3.4 Rinse (30 minutes) in deionized water.

3.5 Rinse in methyl alcohol.

3.6 Dry in air.

## APPENDIX B

### ALKALI METAL LOADING PROCEDURE AND BRAZE-RELATED-MATERIALS ANALYSES

- I. Alkali Metal Loading Procedure
- II. Beryllia Lot Analyses
- III. Columbium-1% Zirconium Analyses
- IV. Interstitial Analyses of Active-Metal  
Braze Alloys
- V. Analyses of 60%Zr-25%V-15%Cb Braze  
Alloy Lots
- VI. Analysis of Yttria Fired Ceramic

## ALKALI METAL LOADING PROCEDURE

The welding of the columbium-1% zirconium capsules and loading of these capsules with test assemblies and with potassium or lithium were carried out under vacuum in a chamber with appropriate fixtures and accessories. (See Section II-B.)

The chamber was a General Technology Model Mark 5A modified to accommodate the special accessories for electron-beam welding and alkali metal loading. The evacuation system consisted of a 15 cfm Welsh forepump, Model No. 1397B; and 1500 liter/sec diffusion pump, NRC Model No. HK6; with a Freon 12 cooled chevron ring baffle, CVC Model No. BCRU60.

The welding equipment consisted of a BTI (Brad Thompson Industries) 6 kW power supply and electron beam gun (BTI No. 786). The gun was mounted on a support boom (BTI No. 215-7) providing X, Y, and Z translation; the X motion being power driven. A modified power driven, variable speed turn-table (BTI No. 1920-12) and manipulators (MCR No. V4-120) completed the modified handling apparatus.

The alkali metal loading sequence was as follows:

1. Weigh capsules and record for later use in potassium fill determination.
2. Argon flush the monitor line until the level is below 10 ppm.
3. Argon flush through the bubbler (about 5 bubbles/sec) for one day before loading.
4. Pull vacuum on and alcohol leak check all fittings into hot trap (fore vacuum pump only required). The hot trap valve and all-metal valve into electron-beam welding chamber remain closed.
5. Vacuum is pulled on the electron beam welding chamber. Vacuum must be better than  $6 \times 10^{-6}$  torr.
6. The argon cover gas is adjusted to one bubble/sec. (prior to hot trapping).
7. Vacuum is pulled on the fill line (prior to hot trapping).
8. Alkali metal is hot trapped at 1400°F for 24 hours (prior to loading).

9. Chemically clean, as required, all parts for the loading sequence.
10. The capsules, test samples, lids and all other parts which could contact the alkali metal or capsule interior are fired to approximately 1300°F in a vacuum of better than  $1 \times 10^{-5}$  torr; then cooled, back-filled with a helium atmosphere and transferred into the loading chamber just prior to the loading operation.
11. The electron-beam welding chamber is flushed with helium. The manipulator flange is opened and adjusted to a helium flow of 20 CFH.
12. The chill blocks, positioning fixtures, and other accessories in the chamber are checked and positioned.
13. Parts are loaded into the electron-beam welding chamber.
14. The electron-beam welding chuck position is checked.
15. The fill line positioning jig location is checked.
16. The location of all loaded items are checked to assure easy manipulator retrieval.
17. The parts list is checked before sealing up electron-beam welding chamber.
18. The valve to the potassium fill line is closed then the roughing valve into the diffusion pump is opened to rough out chamber.
19. When the roughing vacuum is down to  $< 0.1$  torr, the valve to the fill line is opened again.
20. The cold trap refrigeration unit is started.
21. After 5 minutes the diffusion pump is turned on.
22. The potassium fill line is heated to 482°F with heating tapes and Calrod element. The valve into the hot trap and valve into the electron-beam welding chamber remain closed.
23. Start cooling hot trap to 300°F (for potassium).

24. Wait until the pressure reaches  $8 \times 10^{-6}$  torr (not over  $1 \times 10^{-5}$  torr) before proceeding.

Note: Up to this point, if at any time a problem arises, the sequence may be stopped with little loss of time. Once the potassium has been forced into the fill line, associated clean-up time makes it desirable to continue the loading through completion.

25. Cool all parts of the transfer line to 212°F for potassium (392°F for lithium).
26. Close the all-metal valve between the fill line and the rough vacuum line.
27. Close bubbler valve on hot trap cover gas line and pressurize hot trap to 10 psi with argon.
28. Open hot trap liquid metal valve.
29. With appropriate waste receiver in place, the potassium transfer line is flushed with approximately 2 volumes of potassium (or lithium) by opening all-metal valve into electron-beam welding chamber.
30. Carry out appropriate loading and welding sequences to accomplish the purpose of the specific loading.

TABLE B-1. Beryllia Ceramic Lot Designation and Analysis

Lot No. (a)	Ceramic	Form of (b) Ceramic Received	Density (d) (g cm <sup>3</sup> )	Impurity Content (c)																Notes
				Al	Fe	Cr	Ni	Mn	B	Ca	Li	Cu	Mo	Na	Mg	Si	Pb	Ti	Zn	
BeO-A	Thermalox 998 (99.8% BeO)	MoR, VT cyl.	2.85-2.88	60	65	12	10	2	1	65	2	2	< 3	50	700	65	2	3	< 20	(e) (f)
				70	50	< 3	8	2	< 1	210	2	4	< 3	30	850	75	< 2	3	< 20	(g)
				70	45	8	8	2	< 1	75	2	< 2	< 3	30	620	75	< 2	3	< 20	(f) (h)
BeO-AA	Thermalox 998	4" x 4" cyl.	2.85-2.88	Same as BeO-A																
BeO-B	Thermalox 998	MoR, VT cyl.	2.85-2.94	45	70	8	3	3	1	80	2	6	< 3	40	1110	30	< 2	10	< 20	(e)
				65	100	10	8	< 2	< 1	60	2	< 2	< 3	30	1110	65	< 2	3	< 20	(h)
BeO-BA	Thermalox 998	MoR, VT cyl.	2.85-2.94	Same as BeO-B																
BeO-BB	Thermalox 998	2" x 1 2" cyl.	2.85-2.94	Same as BeO-B																
BeO-C	Thermalox 998	2" x 1/2" cyl.	2.89-2.93	80	140	8	12	3	1	85	3	2	< 3	80	1150	50	2	15	< 20	(e)
BeO-D	Thermalox 998	VT cyl.	2.85-2.94	120	60	4	8	2	< 1	210	2	4	< 3	30	750	100	< 2	4	< 20	(e)
BeO-E	Thermalox 998	MoR	2.85-2.93	290	65	7	8	7	1	85	3	4	< 3	80	1200	150	< 2	4	< 20	(e)
BeO-EA	Thermalox 998	MoR	2.85-2.93	Same as BeO-E																
BeO-F	Thermalox 998	MoR		80	60	12	15	2	1	80	3	2	< 3	100	1440	70	< 2	2	< 20	(e)
BeO-G	Thermalox 998	2" x 2" cyl.	2.95-2.96	60	50	8	5	2	< 1	60	3	2	< 3	60	1050	120	2	4	< 20	(e)

- (a) The first letter refers to a purchase from a single manufacturer's lot for which the lot analysis is given.  
The second letter refers to other purchases from the same manufacturer's lot. All beryllia ceramics were from the Brush Beryllium Company.
- (b) MoR - Modulus of rupture bars. 0.1" x 0.1" x 1" long; VT cyl. = vacuum test or creep cylinders 0.4" OD x 0.3" ID x 0.1" long.
- (c) Analysis by emission spectrograph; constituents given in parts per million.
- (d) Reported by vendor.
- (e) Analysis of ready-to-press powder.
- (f) Average of 3 samples.
- (g) Analysis after firing in platinum crucible.
- (h) Analysis after kiln firing.

The maximum amount of sodium in these lots was 100 ppm.  
The maximum amount of sodium in these lots was 100 ppm.  
The maximum amount of sodium in these lots was 100 ppm.

# COLUMBIUM - 1% ZIRCONIUM ANALYSES

TABLE B-2. Analysis<sup>(a)</sup> of Columbiu-1% Zirconium Products Used in Various Applications

Content (ppm) (b)	Product and Heat Number										
	52061-S3B (c)					8-32151 (d)		912-900 (d)		52036 (e)	
	Ingot		Sheet	Plate	Bar	Ingot		Ingot		Ingot	
	Top	Bottom				Top	Bottom	Top	Bottom	Top	Bottom
Zr	0.97%	0.86%	70/90 (f)	50	70	1.00	0.96	1.2	1.10	0.82%	0.90%
C	40	50				60	40	30	35	50	50
Li	25	20				35	43	89	135	35	30
O	<50	<50				210	190	280	290	<50	<50
H	2.5	2.3				5	4.2	2.0	2.4	4.5	4.2
Ta	<500	<500				800	940	(g)	(g)	<500	<500
W	350	320				360	380	<300	<300	70	90
Al	<20	<20				25	35	(g)	(g)	<20	<20
B	<1	<1				<1	<1	<1	<1	<1	<1
Cd	<5	<5				<5	<5	<5	<5	<5	<5
Co	<10	<10				<10	<10	<20	<20	<10	<10
Cr	<20	<20				<20	<20	(g)	(g)	<20	<20
Cu	<40	<40				<40	<40	(g)	(g)	<40	<40
Fe	<50	<50				54	<50	<100	<100	<50	<50
Mg	<20	<20				<20	<20	(g)	(g)	<20	<20
Mn	<20	<20				<20	<20	(g)	(g)	<20	<20
Mo	500	500				150	150	<20	<20	35	25
Ni	<20	<20				<20	<20	<20	<20	<20	<20
Pb	<20	<20				<20	<20	<20	<20	<20	<20
Si	<50	<50				80	100	<100	<100	<50	<50
Sn	<10	<10				<10	<10	(g)	(g)	<10	<10
Ti	<40	<40				<40	<40	<150	<150	<40	<40
V	20	20				<20	<20	<20	<20	<20	<20
Hf	<80	<80				<80	<80	(g)	(g)	<80	<50
Cb	Remainder					Remainder		Remainder		Remainder	

- (a) Analysis on ingots and final products supplied by the vendor, Wah Chang, Inc.  
 (b) Content shown in ppm unless otherwise indicated.  
 (c) This heat in the form of sheet and plate was used in the fabrication of test assemblies and capsule tops and bottoms.  
 (d) Tubing made from this ingot was used in making alkali metal purity test capsules.  
 (e) Tubing made from this ingot was used in making specimen test capsules.  
 (f) Oxygen content of sheet in the as-rolled condition was 90 ppm; in the rolled and annealed condition, oxygen content was 70 ppm.  
 (g) Not determined.



# INTERSTITIAL ANALYSES OF ACTIVE-METAL BRAZE ALLOYS

TABLE B-3. Interstitial Content of Selected Active Metal Brazing Materials in Button, Powder and Foil Form (g)

Material	Form	Oxygen (ppm)	Nitrogen (ppm)
Be (a)	--	2500 (b)	200
Th (a)	--	600	60
Ti (a)	--	180	20
Y (a)	--	2000-4000	100
Zr (a)	--	0- 360	6-36
V (a)	--	784	270
56Zr-28V-16Ti	Melted button (c)	580	100
	Powder (c)	620	120
	Foil (c)	1700	1000
60Zr-25V-15Cb	Melted Button	520	97
	Powder	960	98
65V-35Cb	Melted Button	900	260
	Powder	990	260
50Ti-30Zr-20V	Powder	710	(f)
	Foil	2600	(f)
40Zr-30Ti-30V	Powder	(f)	(f)
	Foil	1300	(f)
V (d)	Foil	1600	360
Zr (e)	Foil	850	25

(a) Typical analyses supplied by Battelle Memorial Institute on raw materials used in preparation of the listed active alloy braze materials which they supplied in button, powder or foil form.

(b) As BeO

(c) The powder and foil were from a different melt than the button.

(d) Foil supplied by Battelle Memorial Institute

(e) Foil supplied by Wah Chang.

(f) Not determined

(g) All analyses except those materials marked (a) were made by Westinghouse R & D Center. Oxygen by vacuum fusion; nitrogen by modified Kjeldahl.

# ANALYSES OF 60%Zr-25%V-15%Cb BRAZE ALLOY LOTS

TABLE B-1. Analyses<sup>(a)</sup> of Several Lots<sup>(b)</sup> of 60Zr-25V-15Cb Braze Alloy

Material	Form	Major Constituents (weight percent)			Interstitials (ppm)		Variation in Interstitials Relative To Button Lot E (ppm)	
		Zr	Cb	V	O	N	O	N
60Zr-25V-15Cb Lot E	Powder (-50 mesh)	59	14.8	25	2310	100	+1880	-30
60Zr-25V-15Cb Lot E	Button	60	14.9	25	430	130	0	0
60Zr-25V-15Cb Lot F	Powder (-60 mesh)	--	--	--	2150	280	+1720	+150
60Zr-25V-15Cb Lot F	Button	41	15.8	42	1100	260	+ 670	+130
60Zr-25V-15Cb Lot D	Powder (-50 mesh)	60	15.0	24	--	--	--	--

(a) Constituent Analyses by x-ray fluorescence method; all analyses by Westinghouse R & D Center except Lot D which was analyzed by the Varian Labs. Interstitial analyses were made by the Westinghouse R & D Center; oxygen by vacuum fusion, nitrogen by micro Kjeldahl.

(b) Braze Alloy Lots D & E were supplied by Battelle Memorial Institute; Lot F was supplied to EIMAC for an internal program by Materials Research Corporation. Lots D and E were used in the fabrication of specimens on this program. Modulus of rupture specimens made with Lot F were strength tested before the analysis was completed. MOR tests indicated flexural strength very similar to that obtained with Lots D and E. (21,600 psi for Lot F and 22,170 psi for Lot D. Standard deviations were 2200 psi and 2850 psi respectively.) However, no further specimens or tests were made with Lot F of the braze alloy on this program.

# ANALYSIS OF YTTRIA FIRED CERAMIC

TABLE B-5. Analysis of Yttria Fired Ceramic

Element	Amount Detected (a)
Al	30 ppm
Si	40 ppm
Ca	each < 30 ppm
Cr	
Sr	
Ba	
Cd	
B	
As	
Tl	
Sn	
Co	
Be	
Sb	
Hg	
P	
Zr	
Mn	
Pb	
Ge	
Mg	
W	
Ni	
Fe	
Bi	
Mo	
V	
Ti	
Li	
Cu	
Ag	
Na	
Zn	

Note: (a) Total impurities estimated to be less than 200 ppm. Data from Coors Porcelain Company. (Spectrographic Analysis)

## APPENDIX C

### FLEXURAL STRENGTH OF BERYLLIA CERAMICS

A detailed, statistical study of the strength of high purity beryllia as a function of temperature was reported by B. A. Chandler and associates in the Journal of Nuclear Materials Vol. 8, No. 3, 1963. The reader is referred to this report for detailed high temperature strength properties of beryllium oxide.

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